A KINETIC STUDY OF SOME FREE RADICAL POLYMERISATION REACTIONS.

A Thesis submitted to Glasgow University in accordance with the regulations governing the award of the degree of Doctor of Philosophy by William Henderson, B.Sc.

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November, 1962.

S U M M A R Y.

In part one of this thesis some of the methods of determining the rate of initiation in a polymerisation reaction proceeding by a free radical mechanism have been studied and compared. All of the measurements relate to the photoinitiated polymerisation of methyl methacrylate in bulk using 1:1' azobis - isobutyronitrile (AIBN.) as the initiator.

The stable free radical, 1:1' diphenyl - 2 - picrylhydrazyl, (DPPH.), has frequently been used as an inhibitor in polymerisations. The rate of removal of DPPH. has been measured and equated to the rate of initiation. The rate of disappearance of DPPH. has been followed dilatometrically and spectrophotometrically and DPPH. has also been used as a radical scavenger in an inert solvent.

The rate of initiation has also been evaluated from the number average degree of polymerisation and the rate of polymerisation. The kinetic chain length has been measured, and it is shown that an unambiguous

value for the rate of initiation can be obtained from the value of the kinetic chain length together with that of the rate of polymerisation.

The values obtained using DPPH. and by measurement of the kinetic chain length have been compared and the differences have been explained in terms of the efficiency of initiation of polymer chains by AIBN. An efficiency of about 60% has been found.

The kinetic chain length and the number average degree of polymerisation have been compared and it is confirmed that the termination process between polymethyl methacrylate radicals occurs mainly by disproportionation at 25°C.

In part two of this thesis the photoinitiated polymerisation of 2 - vinyl pyridine using AIBN. as initiator has been reported. A brief examination of the polymerisation of 4 - vinyl pyridine has also been made. For 2 - vinyl pyridine, the dependence of the rate of polymerisation on the initiator concentration and the intensity of irradiation has been studied for the initial stages of reaction (6% poln.) and can be expressed:-

$$\text{Rate} = K.[\text{AIBN}]^{0.5} n^{0.5}$$, where K is a constant, $[\text{AIBN}]$ = initiator concentration, and n is the intensity of irradiation.

The rate of initiation has been measured from the kinetic chain length. An attempt to use DPPH.

to measure the rate of initiation was unsuccessful.

The velocity coefficients for the propagation and termination reactions have been evaluated by the non - stationary state thermocouple method and by the rotating sector technique.

The activation energy for both the propagation and termination reactions and the heat of polymerisation have also been measured.

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A C K N O W L E D G E M E N T S .

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I N D E X.

PART ONE.

P A R T ONE.

A STUDY OF SOME METHODS OF MEASURING THE RATE OF INITIATION IN A POLYMERISATION REACTION.

C H A P T E R I.

INTRODUCTION.

Staudinger[1] in 1920 published a paper in which he proposed chain structures for polymeric materials. He assigned structures of the form

$$-CH_2-\underset{\displaystyle C_6H_5}{CH}-CH_2-\underset{\displaystyle C_6H_5}{CH}- \quad , \quad -CH_2-O-CH_2-O-CH_2- \quad , \text{ etc.}$$

for polystyrene and polyoxymethylene. These structures are still accepted today. Staudinger pointed out that in contrast to association colloids, high polymers display colloidal properties in all the solvents in which they dissolve.

A mechanism for polymerisation was suggested in which intermediate structures were regarded as having a free valency at each end. Staudinger considered that activation of the monomer resulted in the opening of a double bond, and that the activated molecule reacted with successive units of

monomer to give intermediate structures. He suggested that the termination process occurred simply by deactivation of growing radical by virtue of its great length.

The first complete free radical mechanism for a polymerisation was given by Taylor & Jones[2] in 1930. Another scheme had been suggested previously by Whitby & Kantz[3], who, while they accepted the idea of linear polymeric molecules, did not agree with Staudinger's concept of free radical intermediates. They postulated a mechanism involving successive hydrogen transfer between a polymeric molecule and the vinyl monomer.

The concept of free radical polymerisation was ultimately accepted when it was shown that polymerisation could be initiated by substances which were known to decompose to give radicals on photo - excitation. There have been major advances in the manufacture and applications of synthetic polymers which have resulted from the realisation that these are not merely substitutes, but may offer a combination of properties markedly superior for certain purposes, by comparison with conventional materials.

The search for new polymers has provided the incentive for investigations into the fundamental chemical processes by which polymers are formed.

Such investigations have in their turn resulted in advances in theoretical chemistry, an outstanding example being the chemistry of free radical reactions, the quantitative development of which owes much to polymer chemistry.

A polymer molecule may be regarded as a permanent record of the chain reaction in which it was formed. The size, shape, and composition of the molecule, and the nature of its end - groups, are all controlled by the relative rates and mechanisms of the elementary steps into which the whole process can be divided. Kinetic studies of a polymerisation reaction and examination of the resulting polymer can lead to a comprehensive understanding of the mechanism of the reactions occurring during polymerisation , and the factors governing their rate. An understanding of the physical chemistry of polymerisation is an obvious prerequisite to the ultimate objective of the preparation of polymers with prescribed structures and properties.

It is now realised that there are three separate stages which are fundamental to any free radical polymerisation reaction. These are initiation, propagation, and termination. The kinetic scheme, based on these reactions, may be represented:-

	$C \rightarrow C'$	Rate.	...(1.1)
INITIATION.	$C' + M \rightarrow R_1'$	I	...(1.2)
PROPAGATION.	$R_n' + M \rightarrow R_{n+1}'$	$K_p[R][M]$	...(1.3)
TERMINATION.	$R_n' + R_m' \rightarrow P_{n+m}$	$K_t[R]^2$	...(1.4)
	or $P_n + P_m$		

where C, M, and P represent molecules of initiator, monomer, and inactive polymer respectively. Free radicals are indicated by a dash, i.e.,('). Square brackets signify the concentration of the reactant.

The initial free radical (1.1) may be generated either thermally or photochemically from a molecule of monomer, or may be obtained from a molecule of catalyst, i.e. the initiator, as in a sensitised polymerisation. Reaction (1.2) is the true initiation step in polymerisation: the initial radical combines with a molecule of monomer forming a growing polymer radical. The propagation reaction (1.3) involves the the rapid addition of a large number of monomer molecules, one at a time, to the radical formed in the initiation reaction. The termination reaction (1.4) is the step in which the growing polymer radicals are deactivated to give stable polymer molecules. Two mechanisms of termination are possible. The growing polymer radicals may combine to give a larger polymer molecule, each radical contributing

one electron to form a covalent bond, or, alternatively, disproportionation may occur, one polymer molecule having an unsaturated end - group and the other a saturated end - group.

A further process may occur in some systems - a chain transfer reaction. This may be represented:-

CHAIN TRANSFER. $R_n' + X \rightarrow P_n + X'$ ... (1.5)

where X represents a molecule of monomer, polymer, or an initiator radical.

From the basic kinetic scheme set out on page 4, and assuming that chain transfer is unimportant in a particular polymerisation reaction, a simple equation may be derived for the overall rate of reaction.

The only reactions which involve the consumption of free radicals are the initiation and termination steps, and therefore the rate of change of radical concentration can be expressed:-

$$d[R]/dt = I - K_t[R]^2 \qquad \ldots(1.6)$$

and when stationary state conditions apply, i.e., when the rate of formation of radicals is equal to the rate of consumption of radicals, then:-

$$d[R]/dt = d[R_s]/dt = 0 \qquad \ldots(1.7)$$

where $[R_s]$ represents the steady concentration of radicals during the stationary state period of the polymerisation reaction.

Reaction (1.3) is the only step involving

appreciable consumption of monomer, and if the rate of polymerisation is expressed in terms of the rate of removal of monomer, then:-

$$-d[M]/dt = K_p[R][M] \quad \ldots(1.8)$$

$$= K_p[R_s][M], \text{ assuming} \quad \ldots(1.9)$$

$$= K_p \frac{I^{0.5}}{K_t^{0.5}}[M] \text{ stationary state.} \quad \ldots(1.10)$$

This is the basic equation governing all free radical polymerisation reactions which conform to the simple kinetic scheme given on page 4. The rate of polymerisation is thus a composite function of the velocity coefficients of the separate steps in the overall reaction. In those cases where other reactions also occur, e.g., a chain transfer reaction, the basic equation must be modified.

In attempting to relate experimental results of a polymerisation reaction to the simple kinetic scheme it is usual to make the following assumptions:-

a) The reactivity of the growing chains is independent of chain length.

The free radical intermediates in a vinyl polymerisation are all of a similar nature, but differ from one another in the number of monomer units from which they have been formed. The kinetic treatment must consider radicals of all sizes and it has been

the practice to assume that the reactivity of any given radical is independent of its length. Thus one velocity coefficient can be used to describe all termination steps or to characterise all chain transfer reactions between the growing polymer radicals and any other single species, and only one velocity coefficient is necessary to define all the propagation reactions which occur. This assumption leads to kinetic equations which are in agreement with the majority of results which have been found in vinyl polymerisations.

It should be noted however that recent work by Kirkham & Robb[4] indicates that the assumption of equal reactivity is incorrect, at least for the first few units of monomer which are added.

b) The rate of polymerisation is equal to the rate of propagation.

The overall rate of reaction is generally taken as the rate of removal of monomer in the propagation step neglecting any consumption of monomer in initiation or chain transfer reactions since this will be negligibly small where high polymer is produced.

c) Stationary state conditions are set up quickly.

The concentration of reactive radical intermediates is supposed to remain constant during

the polymerisation reaction.[5] This approximation obviously cannot apply to the very earliest part of the reaction, but can be successfully used over most of the reaction, during which period the concentration of reactants remains virtually constant.

One of the major tasks of the polymer chemist is to assign definite values to the rate constants K_p and K_t and to determine the importance of any chain transfer reactions which occur, and to evaluate the rate of initiation. A clear understanding of the overall process of polymerisation is impossible without a knowledge of at least the order of magnitude of the velocity coefficients of the individual reactions. The behaviour of different monomers is also most usefully compared by examining the ratios of the velocity coefficients in each system. From an industrial viewpoint, the knowledge of the velocity constants and the activation energies of the individual steps is essential for the successful design of efficient plant for the production of synthetic polymers.

As will be shown later, the evaluation of the rate of initiation is an integral part of the determination of the constants K_p and K_t. Any inaccuracy in the determination of the rate of initiation will therefore be reflected in the values

of the constants so derived. Apart from this however, a knowledge of the rate of initiation is of interest for other reasons, for example, in the calculation of quantum efficiency in photo - initiation and the efficiency of initiation in a sensitised polymerisation.

The object of Part 1 of this thesis is to make a comparison of some of the methods of measuring the rate of initiation. In the past various methods have been used for measuring the rate of initiation, but few comparisons of the various methods have been reported. There has therefore been considerable uncertainty about values of the rate of initiation in some systems, and doubt exists regarding the interpretation of experimental results for the determination of the rate of initiation by some methods.

In this work the well known monomer methyl methacrylate was chosen as a suitable monomer for examination of the rate of initiation as determined by several methods since it is known to conform to the simple kinetic scheme given on page 4 and little chain transfer with polymer or monomer occurs, at least during the first few percent reaction. Other factors which were responsible for its choice were the ease with which the monomer can be purified and handled.

All polymerisations were carried out photochemically using 1:1' azobisisobutyronitrile as initiator. In such a system the rate of initiation is a function of the rate of decomposition of the initiator which in turn depends on the initiator concentration and the intensity of irradiation. In photochemical initiation temperature has very little effect over the useful range in which the initiator is generally employed.

If the rate of initiation and the rate of decomposition are known, the efficiency of initiation may be calculated. Thus:-

$$\text{Efficiency} = \frac{\text{Rate of Initiation}}{n.K_d[\text{Initiator}]}, \text{ where}$$

K_d is the velocity coefficient for the decomposition of the initiator and n. is the number of radicals produced from one molecule of initiator. n. is normally two, but in some cases it may be one (e.g. in systems involving an electron transfer). The constant K_d refers to the primary dissociation of the initiator and not necessarily to the total rate of consumption of initiator which may include contributions from further decomposition of the radicals initially formed.

Efficiencies of less than 100% may occur in

two ways:

1) the initiator may decompose partly by a non - radical mechanism to give products which cannot initiate polymerisation, or,

2) some of the radicals may not initiate polymer chains, but take part in other reactions. This radical wastage might result from:-

a) direct interaction of the radicals derived from the initiator;

b) a termination reaction involving a polymer radical and an initiator radical, i.e., primary radical termination;

c) reaction of the radical with another component of the system.

Measurements of rates of initiation using 1:1' azobisisobutyronitrile by a variety of techniques has led to an efficiency of about 60% for many systems. Bamford et als.[6] give values of 0.79 and 0.58 for the polymerisations of acrylonitrile and styrene respectively in NN-dimethylformamide solution at 60°C, using the ferric chloride technique. The latter value is in good agreement with results by Bevington[7] who used a tracer technique. Calculations of the relative rates of initiation reactions and those reactions by which radicals may be wasted, assuming reasonable velocity coefficients indicate that

initiation should be favoured except when the initiator concentration is low. The comparatively low efficiencies are generally explained in terms of a"cage effect" in which the solvent or monomer molecules are assumed to form a barrier which effectively hinders the separation of newly formed radicals and so encougages their interaction.

Noyes[8] has approached this problem from a different stand - point. He comments that ordinary kinetic principles cannot be applied to the interpretation of the two reactions:-

$$2R' \rightarrow R_2 \qquad \ldots(1.11)$$

$$\text{and} \quad R' + M \rightarrow RM' \qquad \ldots(1.12)$$

since the distribution of R' radicals is not random. The radicals are generated in pairs and so, until they diffuse apart , the wastage reaction is preferred.

Three types of recombination are possible:-

1) Primary recombination occurs within about 10^{-11} sec. after the generation of the radicals and before they have had time to diffuse apart by more than a molecular diameter;

2) Secondary recombination occurs within about 10^{-9} sec. of dissociation, so that although the radicals have separated to some extent there is still a finite possibility that re - encounter may occur;

3) Recombination in the body of the solution may occur between radicals which have escaped primary and secondary recombination and also reaction with a radical scavenger. This reaction will almost certainly involve radicals originating from different molecules of initiator.

Primary and secondary recombination may together be referred to as cage recombination, but the term used by Noyes is "geminate" recombination, which suggests the interaction of radicals derived from the same molecule of initiator.

The use of an unsymmetrical azo initiator which gives radicals of the types R_a' and R_b' might be helpful in studying the various types of recombination. Geminate recombination would produce products of the type $R_a.R_b$ and at low monomer concentrations where recombination in the body of the solution becomes significant, the products $(R_a)_2$ and $(R_b)_2$ should also be formed. It is appreciated that the determination of these products in the very low concentrations in which they would occur would be extremely difficult, but the problem could perhaps be approached by using a C^{14} labelled initiator and the isotope dilution technique.

There are several methods for measuring the rate of initiation in a polymerisation, but no one

method is ideally suited to all cases. There are two main classes into which the various methods can be assigned:-

a) estimation of the rate of production of free radicals by addition to the polymerisation system of a foreign substance which reacts with free radicals and whose rate of disappearance can be followed by physical or chemical means. The use of inhibitors and retarders falls into this class.

It is also convenient to consider under this heading measurement of the rate of decomposition of an initiator in an inert solvent by a radical scavenger. It must be realised that any rate of initiation measurement based on the measurement of the rate of decomposition of the initiator in an inert solvent will be subject to a measure of uncertainty because of doubts concerning the efficiency of initiation.

b) calculation of the rate of initiation from other measured kinetic quantitites, e.g., from rate of polymerisation and degree of polymerisation, or from kinetic chain length.

METHODS OF MEASURING THE RATE OF INITIATION.

a) Methods involving the addition of a foreign substance to the polymerising medium, and measurement of its rate of disappearance.

When a substance is added to a polymerising vinyl monomer it may function in a variety of ways in addition to acting as a diluent. The effects produced on the rate of polymerisation may be:-

Initiation - an increased rate of reaction occurs;

Retardation - the rate of polymerisation is reduced but not completely suppressed;

Inhibition - the added substance causes complete suppression of polymerisation.

All of these additives result in a change in the degree of polymerisation of the polymer formed. A further class of additives has no specific effect on the rate of polymerisation but reduces the degree of polymerisation much more than can be explained by simple dilution. These materials are termed chain transfer agents.

Substances which cause inhibition or retardation may be used to determine the rate of production of free radicals in a polymerisation reaction. For inhibition it is necessary that the added substance should react preferrentially with the primary

initiating radicals and it is desirable that the rate of polymerisation after inhibition should be close to the rate produced in the absence of inhibitor. For ideal inhibition kinetics the length of the inhibition period should be proportional to the concentration of inhibitor.

The choice of an inhibitor which is of general usefulness is very restricted since a wide range of substances show retarding effects rather than inhibition. Further, some inhibitors are specific or selective in action. Thus, benzoquinone inhibits the polymerisation of vinyl acetate[9] but only retards the polymerisation of methyl methacrylate[10]. As reported in Part 2 of this work it shows little effect on the polymerisation of 2 - vinyl pyridine. Inhibition and retardation are basically similar reactions, the chief difference being in the relative rates of the two processes.

The most useful classification of retarders and inhibitors is according to the way in which they react with radicals. On this basis three types of additive can be distinguished:-

i) stabilised free radicals which react with radicals present in polymerising systems, but not with the monomer;

ii) substances which are essentially transfer

agents but the products of radical displacement are so unreactive that they initiate very inefficiently; iii) substances to which primary or polymer radicals become chemically attached giving new radicals which are relatively unreactive.

From equation (1.10) it is seen that the rate of polymerisation may be decreased by reducing I, the rate of initiation. The simplest way in which this can be effected is by the addition to the system of a substance which will react with the initiating or propagating radicals to give products which are inert, or new radicals which are incapable of initiating as readily as the original radical species. Since the reactivity of the new radical relative to the original species may vary from unity to almost zero, it is evident that similar mechanisms could operate in both retardation and inhibition.

The simplest type of inhibition is that resulting from the addition of a stable free radical which combines with the initiating or propagating radical to give an inert product. The inhibitor need not be a free radical however, since the added substance, Z, may react in several ways[11,12]. The initial reaction between Z and the radical may be either:-

1) direct addition to give a larger radical,

$$R' + Z \rightarrow RZ' \qquad K_z \qquad \ldots(1.13)$$

or,

2) a transfer reaction such as

$$R' + Z \rightarrow P + Z' \qquad K_{sz} \qquad \ldots(1.14)$$

Reaction (1.13) is formally possible if Z is an unsaturated, aromatic or cyclic compound, and also if the reaction involves complex formation[13].

A further type of reaction similar to (1.14) can take place with certain metallic halides[14]. Thus when ferric chloride is used with certain types of polymer radical a reaction of the following type can occur:-

$$R' + FeCl_3 \rightarrow P + FeCl_2' \qquad \ldots(1.15)$$

Monomers which have been used include styrene, acrylonitrile, methacrylonitrile, methyl acrylate, and methyl methacrylate in non - aqueous solution. The nature of the anion is of some importance. Entwistle[15] has studied a wide range of ferric salts and has shown that while ferric chloride only retards the polymerisation of methyl methacrylate ferric bromide is an excellent inhibitor.

In the case of reactions (1.13) and (1.14) the new radical formed may undergo a variety of subsequent reactions including;

i) termination by combination or disproportionation;

ii) transfer with the monomer or the added substance;

iii) propagation with the monomer, or less probably, with the added substance. The molecules produced in these reactions may be inert or may participate further in any of the usual steps of vinyl polymerisation, some of which may result if the regeneration of an inhibitor molecule.

It will be appreciated that the problem of elucidating such a complex series of reactions is clearly very difficult, and it is not surprising that few of the proposed mechanisms for inhibition and retardation which can be tested experimentally have been found to be entirely satisfactory.

For an inhibitor or an ideal retarder (one which reacts with the polymer radicals directly to give an inert product) the following kinetic scheme can be set out:

$$C \rightarrow C' \qquad \ldots(1.16)$$

$$C' + M \rightarrow R_1' \quad \text{Rate} = I \qquad \ldots(1.17)$$

$$R_n' + M \rightarrow R_{n+1}' \quad \text{Vel.const. } K_p \qquad \ldots(1.19)$$

$$R_n' + Z \rightarrow \text{Inert products.} \quad K_z \qquad \ldots(1.20)$$

$$R_n' + R_m' \rightarrow P_{m+n} \quad K_t \qquad \ldots(1.21)$$

$$\text{or} \quad P_n + P_m$$

$$\text{Thus,} \quad d[R']/dt = I - K_z[R'][Z] - K_t[R]^2 \qquad (1.22)$$

$$\text{and} \quad -d[Z]/dt = K_z[R'][Z] \qquad \ldots(1.23)$$

$$\text{where } [R'] = \sum_n [R_n']$$

The complete integral of equations (1.22) and (1.23) cannot be obtained in a simple form, and it is not therefore possible to express the radical concentration in terms of the experimental variables except by assuming stationary state conditions and setting $d[R^{\cdot}]/dt = 0$.

In many cases this procedure may not be valid, since the rate of change of radical concentration, as reflected in the rate of polymerisation is experimentally seen to be appreciable.

If the stationary state assumption is applied, then,

$$-d[M]/dt = K_p[R^{\cdot}][M] \qquad \ldots(1.8)$$

$$= R_p \quad \text{say.}$$

From (1.22) and (1.23),

$$\frac{d[R^{\cdot}]}{dt} = \frac{I}{K_p[M]} \times \frac{dR_p}{dt} = I - K_t[R^{\cdot}]^2 - \frac{d[Z]}{dt} \qquad \ldots(1.24)$$

Now since R_p is usually small during an induction period and since K_p is usually of the order of 10 - 1,000 mole.$^{-1}$ l.sec.$^{-1}$, the quantity on the left hand side of (1.24) can be made small compared with both I and the terms in brackets if conditions are suitably chosen, so that the stationary state assumption is in fact reasonable.

In cases where the inhibition period is not

sharply defined, the assumption is less satisfactory, particularly near the end of the inhibition period when dR_p/dt and $d[R']/dt$ are increasing in value.

In the presence of a strong retarder, the rate of mutual termination of polymer chains is small compared with the rate of termination with retarder. This is seen if the stationary state assumption is applied to the induction period, thus:-

$$I = K_z[R'][Z] + K_t[R']^2 \qquad \ldots(1.25)$$

When the inhibitor is exhausted, $Z = 0$ and the concentration of polymer radicals assumes its maximum value R'_{max} as given by:-

$$I = K_t[R'_{max}]^2 \qquad \ldots(1.26)$$

The fraction of the total termination occurring by mutual termination of polymer radicals during the induction period is, from (1.8)

$$\frac{K_t[R']^2}{I} = \frac{K_t[R']^2}{K_t[R'_{max}]^2} = \frac{(R_p)^2}{(R_{p.max})^2} \qquad \ldots(1.27)$$

and is sufficiently small to be neglected. Hence during this period,

$$I = K_z[R'][Z] = -d[Z]/dt \qquad \ldots(1.28)$$

so that measurement of the initial rate of disappearance of Z will allow an estimate of the

rate of initiation to be made.

Kice[16] has given a kinetic scheme which takes into account other possible reactions of the inhibitor molecules or radicals, such as co - polymerisation or chain transfer. His scheme has been successfully applied to the polymerisation of methyl methacrylate[16] and methyl acrylate[17].

The kinetic scheme is represented thus:-

$$\left.\begin{array}{lll}
C \rightarrow C' & & \\
C' + M \rightarrow R_1 & & I \\
R_r' + M \rightarrow R_{r+1}' & & K_p \\
R_r' + Z \rightarrow Z_r' & & K_z \\
Z_r' + M \rightarrow R_{r+1}' & & K_{zp} \\
Z_r' + Z_s' \rightarrow \text{Inert products.} & & K_{tz} \\
Z' + R' \rightarrow \text{Inert products} & & K_{tx} \\
R' + R' \rightarrow \text{Polymer.} & & K_t
\end{array}\right] \quad ..(1.29)$$

By rigorous kinetic treatment Kice was able to show that:

$$\frac{\mu^2 Z}{1-\mu^2}\left[1 + \sqrt{1 + \left[\frac{(1-\mu^2)}{\phi^2\mu^2}\right]}\right] = \frac{K_t R_p}{K_p K_z}\left[1 + \frac{(1-\mu^2)}{\phi^2\mu^2}\right]^{0.5} + \frac{K_{zp}K_t[M]}{K_{tx}K_z} \quad ..(1.30)$$

where $\mu = R_p/R_o$ and $\phi = K_{tx}/(K_t.K_{tz})^{0.5}$ and R_p and R_o are the rates of polymerisation in the presence and absence of Z respectively.

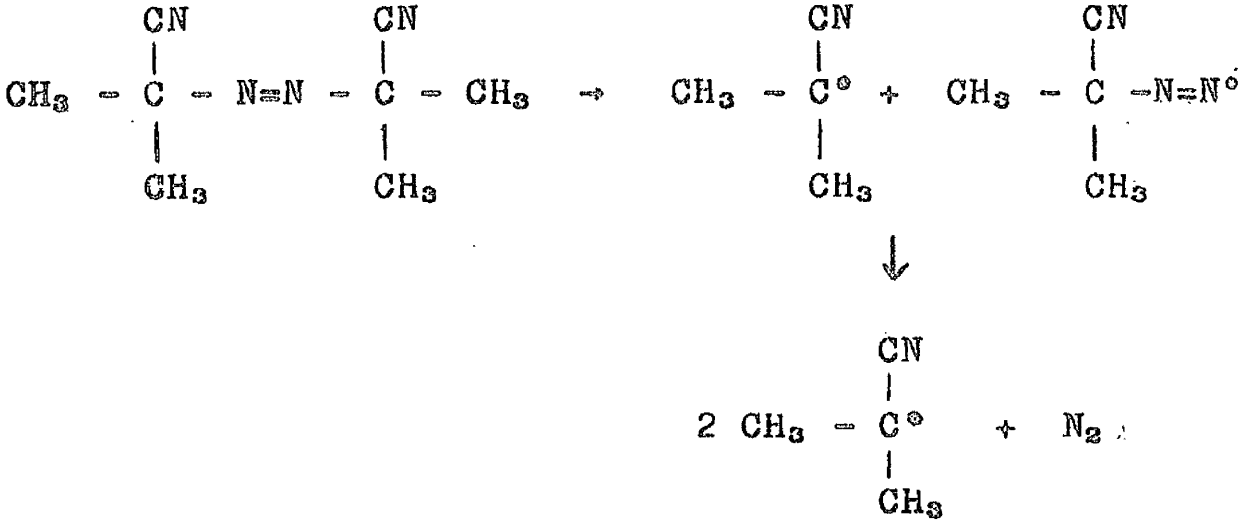
The velocity coefficients for reaction between a number of retarder molecules and radicals derived from methyl methacrylate and methyl acrylate were calculated and it was found that the extent to which benzoquinone participates in co-polymerisation with methyl methacrylate was in agreement with determinations by other methods.

In this thesis the stable free radical 1:1' diphenyl-2-picrylhydrazyl (DPPH.) has been used. It is an inhibitor for the photochemical polymerisation of methyl methacrylate and has a characteristic purple colour in solution in many organic solvents. Its rate of removal can be followed by direct observation of the inhibition period produced or by measuring the change in colour as the reaction proceeds.

The rate of removal of DPPH. has been taken as equivalent to the rate of initiation, i.e., one DPPH. radical has reacted with one initiating radical. This interpretation was put forward by Bawn & Mellish[18] but has subsequently been questioned by a number of other workers[19,20]. It is clear that the rate of removal of DPPH. from any particular system must be

interpreted with care when it is correlated to the rate of initiation.

The initiator 1;1' azobisisobutyronitrile has been shown by kinetic studies to decompose both thermally and photochemically by a unimolecular process:



When 1:1' azobisisobutyronitrile (AIBN.) decomposes in pure solvents the subsequent reactions lead to the formation of tetramethylsuccinodinitrile, isobutryonitrile, etc.[21 - 23]. The radicals generated from AIBN. when it is used to initiate polymerisation show a variable efficiency in various monomers[11,19,24].

Since DPPH. measures the rate of production of available radicals it should give a direct measure of the maximum rate of chain initiation by initiators such as AIBN. Even although AIBN. may decompose at about the same rate in a variety of solvents, its

efficiency may vary from system, e.g., the use of DPPH. indicates that AIBN. is quite inefficient in carbon tetrachloride.

Bawn & Mellish[18] proposed the following scheme for reaction between DPPH. and AIBN. in air saturated solutions.

$$\text{AIBN.} \xrightarrow{K_1} 2(CH_3)C(CN) + N_2 \quad ..(1.31)$$

$$(CH_3)C(CN) + \text{DPPH.} \xrightarrow{K_2} (CH_3)C(CN)\text{-DPPH.} \quad ..(1.32)$$

If (1.32) is very fast, $-d[\text{DPPH}]/dt = 2K_1[\text{AIBN}]$ The values of K_1 obtained were in reasonable agreement with rate measurements by nitrogen evolution. Walling[25] however has pointed out that at 60°C the decomposition rate measured by DPPH. was about 70% of that measured by nitrogen evolution so that not all the radicals generated from AIBN. react with DPPH., but some recombine with their original partners in a "cage reaction".

Lyons & Watson[26] have shown that rate measurements based on DPPH. which has been crystallised from a solvent in the normal manner must be multiplied by a factor to give rates corresponding to pure DPPH. since a complex is formed between DPPH. and the solvent. The difference between the results

of Bawn & Mellish and those found by nitrogen evolution will thus be increased.

The "cage effect" discussed by Walling must be operative within a very short period after the generation of radicals since Flory[27] has shown that on the average a pair of radicals will have separated so far within 10^{-9} sec. that rediffusion together is highly improbable.

Hammond et al.[19] have similarly disputed the scheme of Bawn & Mellish. They suggest that an appreciable fraction of the radicals react with each other before they diffuse apart, since various radical scavengers do not capture decomposition products quantitatively, e.g., butyl mercaptans, DPPH., iodine, and oxygen.

Arnett & Peterson[24] have also shown that not all the radicals generated from AIBN. are available for initiation in polymerisation reactions. They used a C^{14} labelled initiator and found that in the polymerisation of methyl methacrylate the efficiency was 52%

The simplest way in which DPPH. could react would be by direct addition to the isobutyronitrile radicals to give a tetrasubstituted hydrazine. There is however no evidence that this type of reaction occurs to any great extent[27]. In some cases the DPPH. and the radical might disproportionate to give

the hydrazine of DPPH. and an unsaturated product. Braude et al. [28] have shown that DPPH. can abstract a hydrogen atom from some molecules.

Bevington[29] has studied the reaction between DPPH. and AIBN. in solution using radioactive initiator and inhibitor. He concluded that at least 12% of the DPPH. is converted to the hydrazine, and that the products of the reaction of the isobutyronitrile radicals are found to some extent during the inhibition period. This was attributed to the "cage effect" or to the decomposition of some of the AIBN. by a non - radical mechanism It was further noted that the DPPH.-hydrazine formed could also react with isobutyronitrile radicals.

Burnett et al. [30] however have stated that the hydrazine does not react with isobutyronitrile radicals and has little effect on the polymer radicals present in the polymerisation of methyl methacrylate.

Verdin[31] has shown that the DPPH.-hydrazine does undergo reaction with isobutyronitrile radicals in air saturated solutions, and has indicated that the formation of peroxy radicals precludes the use of DPPH. as a primary radical scavenger in the presence of oxygen.

Bawn & Verdin[32] have referred to the work of Bevington[29] in which he compares his data with that

of Bawn & Mellish[18]. From this comparison Bevington suggested that 12% of the DPPH. is converted to the hydrazine, but Bawn & Verdin have shown that comparison of Bevington's data with their more recent studies now indicates that no hydrazine is formed.

Bawn & Verdin propose that the isobutyronitrile radicals react with DPPH. by addition to the para position of one of the phenyl groups, so giving a product containing an N - H bond. Such derivatives were identified by Goldschmidt & Renn[33] and a mechanism for their formation was proposed by Bennington et al.[34]

The proposal of Bawn & Verdin is in agreement with observations by Henglein[35] who found that when polymethyl methacrylate is degraded in the presence of DPPH., some of the DPPH. becomes chemically attached to the polymer, but subsequent treatment of the polymer with lead dioxide restores the DPPH. colour.

Bawn & Verdin propose the following mechanism for the reaction between DPPH. and AIBN. where R' represents an isobutyronitrile radical and brackets ( ) enclose pairs of radicals not yet separated by diffusion

$$R - N{=}N - R \xrightarrow{K_1} (R' + R') + N_2 \quad \ldots(1.33)$$

$$(R' + R') \longrightarrow \text{TMSDN or (IBN + MAN)} \quad (1.34)$$

$$(R' + R') \longrightarrow R' + R' \quad \ldots(1.35)$$

$$R' + \text{DPPH.} \longrightarrow \text{R-DPPH.} \quad \ldots(1.36)$$

$$R' + R' \longrightarrow \text{TMSDN or (IBN + MAN)} \quad (1.37)$$

where TMSDN is tetramethylsuccinodinitrile, IBN is isobutyronitrile and MAN is methacrylonitrile.

Since conventional rate constants do not apply to reactions (1.34) and (1.35), it is assumed that a fraction (f) of the radicals diffuse apart so that their rate of formation is $2K_1(f)$ AIBN. (f) corresponds to the fraction of the radicals which react with DPPH. and is therefore the initiator efficiency. Values of (f) found ranged from 0.37 at 78°c to 0.52 at 40°C.

b) Methods of measuring the rate of initiation based on the evaluation of other kinetic functions of the system.

It is necessary to note the definitions of two fundamental quantities associated with a polymerising system. These are the number average degree of polymerisation, $\overline{DP}_n$, and the kinetic chain length, $\underline{v}$.

The number average degree of polymerisation is defined as the average number of monomer units consumed per polymer chain terminated. In cases where no chain transfer occurs it can be shown that:-

$$\overline{DP}_n = \frac{K_p[R][M]}{K_t[R]^2} \qquad \ldots(1.38)$$

The kinetic chain length, $\underline{v}$, is the number of monomer units consumed per polymer chain started, and by definition,

$$v = R_p/I \qquad \ldots(1.39)$$

where R_p = rate of polymerisation.

Normally the $\overline{DP}_n$ may be equal to or greater than $\underline{v}$. If termination occurs by disproportionation then $\overline{DP}_n = v$, but if the termination step occurs by

combination, then $\overline{DP}_n = \nu$. In many cases termination does not occur entirely by one mechanism. When chain transfer occurs, however, the relationships between $\overline{DP}_n$ and $\underline{\nu}$ given do not apply. In such a case $\overline{DP}_n$ is less than $\underline{\nu}$ and there are more polymer molecules than there are chains initiated.

Measurements of the rate of initiation have frequently been made by determining the rate of polymerisation and the $\overline{DP}_n$ of the polymer formed and using the relationship:-

$$I = R_p / \overline{DP}_n \qquad (1.40)$$

Now unless the precise mode of termination is known, or if both processes occur, the relative extent of each, the calculated rates of initiation may be subject to an uncertainty factor of two.

Care must be taken to ensure that the method of determination of molecular weight of the polymer is one which will give the number average degree oi polymerisation. For a high polymer, the "molecular weight" is defined by the following relationships:-

Number average molecular weight, M_n, is defined as

$$M_n = \frac{\Sigma n_i . M_i}{\Sigma n_i}$$, where M_i is the molecular weight of the polymer radicals which have $\overline{DP} = i$ and n_i is the number of molecules which have $\overline{DP} = i$.

Weight average molecular weight, $\bar{M}_w$, is defined as

$$\bar{M}_w = \frac{\Sigma w_i . M_i}{\Sigma w} = \frac{\Sigma n_i (M_i)^2}{\Sigma n_i . M_i} \quad , \text{ where}$$

w = the total weight of all the polymer molecules, and w_i = the weight of the polymer molecules which have $\overline{DP} = i$. $w_i = n_i . M_i$

Z - average molecular weight, $\bar{M}_z$, is defined as

$$\bar{M}_z = \frac{\Sigma n_i (M_i)^3}{\Sigma n_i (M_i)^2}$$

Viscosity average molecular weight, $\bar{M}_v$, is given by the empirical relationship:

$$[\eta]_{intr.} = K . \bar{M}_v^{\alpha} \quad , \text{ and molecular weight}$$

determinations by viscosity can be calibrated in terms of $\bar{M}_n$, or $\bar{M}_w$, or $\bar{M}_z$.

It should be clearly realised that the three basic molecular weights are not equal in numerical value. For normal polymer samples which contain a wide distribution of molecular weights $\bar{M}_z > \bar{M}_w > \bar{M}_n$, the smaller molecules showing the greatest effect in the case of $\bar{M}_n$.

Average molecular weights of high polymers may be found from suitable physical measurements on very

dilute solutions of the polymer, or in some cases by a method of chemical analysis of the end groups. Chemical methods can not generally be successfully applied where the molecular weight is greater than 25,000, while physical methods are oftem most successful for high molecular weight polymers.

The physical methods employed involve the measurement of osmotic pressure (leading to number average molecular weight), light scattering (giving weight average molecular weight) and sedimentation equilibrium or sedimentation velocity in conjunction with diffusion measurements (giving Z - average molecular weight).

Each of the methods require extrapolation to infinite dilution for rigorous fulfillment of theory. Polymer solutions usually exhibit deviations from their limiting infinite dilution behaviour, even at low concentrations, and hence it is necessary to carry out measurements using solutions of the lowest experimentally permissible concentrations, and also to extrapolate the data to infinite dilution.

Rates of initiation may also be found from rate of polymerisation measurements and the kinetic chain length. The kinetic chain length is obviously

a more useful function since uncertainty about the method of termination is not reflected in the rate of initiation calculated from the kinetic chain length. It should therefore be possible to derive an umambiguous value for the rate of initiation by measuring the kinetic chain length.

The method used to measure the rate of initiation using kinetic chain length and rate of polymerisation data is due to Bevington, Bradbury, and Burnett[36]. The same technique had also been reported by Bevington, Melville, and Taylor[37] in studies on the termination process in polymerisation.

In this method the following conditions should be satisfied:-

i) the composition of the initiating radicals should be known;
ii) direct thermal or photochemical polymerisation should be of negligible extent, otherwise radicals not derived from the initiator will be present in the system;
iii) the radiation emitted by the active initiator must not be sufficient to initiate polymerisation.

All of these requirements are satisfied in the photochemical polymerisation of methyl methacrylate using C^{14} labelled AIBN. as the initiator. The

chemical composition of such a polymer of methyl methacrylate prepared with AIBN. can be represented as:-

$$(C_5H_8O_2)_n(C_4H_6)_m$$, where

n is the average degree of polymerisation, $\overline{DP}_n$, and m is the number of initiator fragments per polymer molecule.

If the initiator fragments are labelled with carbon-14, then:-

$$\frac{\text{Specific activity of carbon in polymer}}{\text{Specific activity of carbon in initiator}} = \frac{4m}{5n + 4m} \quad (1.41)$$

In this expression 4m is very small compared with 5n if the polymer is of high molecular weight, and therefore for a high polymer,

$$\frac{\text{Polymer activity}}{\text{Initiator activity}} = \frac{4m}{5n} \quad \ldots(1.42)$$

Now, the kinetic chain length , i.e., the number of polymer molecules consumed per polymer chain started, is given by n/m, and therefore:-

$$\nu = \frac{4 \times \text{Initiator activity}}{5 \times \text{Polymer activity}} \quad \ldots(1.43)$$

and hence the rate of initiation is given by:-

$$I = R_p \cdot \frac{5 \times \text{Polymer activity}}{4 \times \text{Initiator activity}} \quad \ldots(1.44)$$

C H A P T E R 2.

EXPERIMENTAL.

Materials.

Methyl methacrylate. I.C.I. grade methyl methacrylate containing 0.1% hydroquinone to prevent polymerisation during storage was used. The monomer was washed with small volumes of a 10% sodium hydroxide solution to remove the hydroquinone, after which it was thoroughly washed with distilled water. The monomer was dried with calcium chloride over a period of at least 24 hours. The calcium chloride was changed several times. The monomer was distilled in an atmosphere of nitrogen, and the fraction boiling at 101^{o}C collected. This sample of monomer was transferred to a distillation flask containing a few cryatals of AIBN. and the flask connected to the high vacuum system. The mixture was thorourgly "degassed" and then photochemically polymerised to about 10% conversion.

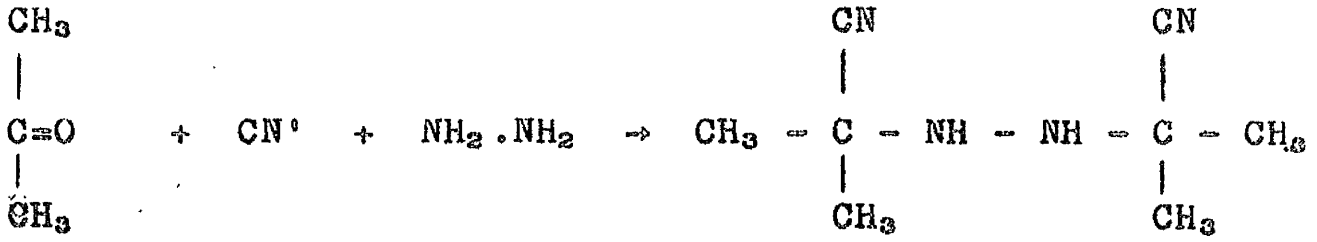
Monomer was then distilled into another flask on the vacuum line and again polymerised to 10% conversion. The monomer was now distilled from this flask into a storage vessel on the vacuum line and kept under vacuum at -78°C.

1;1' azobisisobutyronitrile (AIBN.) Eastman Kodak grade of AIBN. was purified by two recrystallisations from absolute ethanol at 30°C. Particular care was taken not to heat the solution above this temperature to prevent decomposition. The melting point was 102°C.d. Since very small amounts of AIBN. were normally required, it was found convenient to add the AIBN. in the form of a standard chloroform solution.

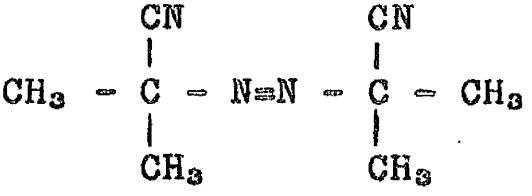
These solutions were stored in darkness and were discarded after one week.

C^{14} labelled AIBN. This was prepared using the method of Overberger et al. [38] Acetone labelled with C^{14}, of 0.1 mc. activity, as supplied by the Radiochemical Centre, was diluted to 10 cc. with analar acetone.

9.3 gm hydrazine sulphate, 7.5 gm of the above active acetone, and 9.4 gm potassium cyanide were mixed in aqueous solution for two days, during which time a crystalline product, the di - substituted hydrazine separated out. Thus:-



This product was filtered off and added to a one litre round - bottom flask together with 50 cc of ethanol and 50 cc of dilute hydrochloric acid. The flask was cooled on an ice bath and stirred during the addition of bromine water, the hydrazine thus being oxidised to give the desired product:-



This was filtered off and recrystallised twice from ethanol.

1:1' diphenyl-2-picrylhydrazyl (DPPH.) This was prepared by the method of Benington et al.[39], which is a modification of the original method of Goldschmidt & Renn[33].

To a solution of 10 gm unsym - diphenhyl-hydrazine hydrochloride in 115 cc of absolute ethanol at room temperature was added 9.5 gm of sodium bicarbonate, followed by 11.3 gm of picryl chloride.

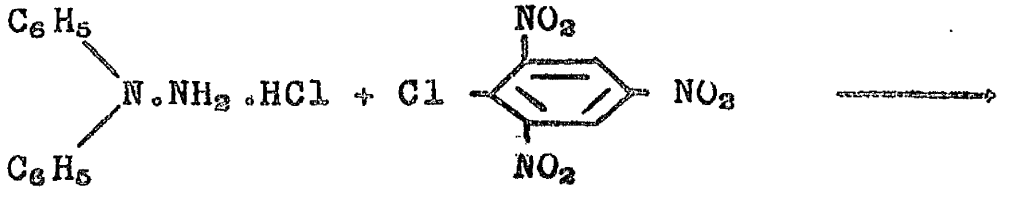
After the evolution of carbon dioxide had ceased, the mixture (now red) was gently boiled for 15 minutes, after which an equal volume of chloroform was added to the mixture while still warm. The solid residue was filtered off.

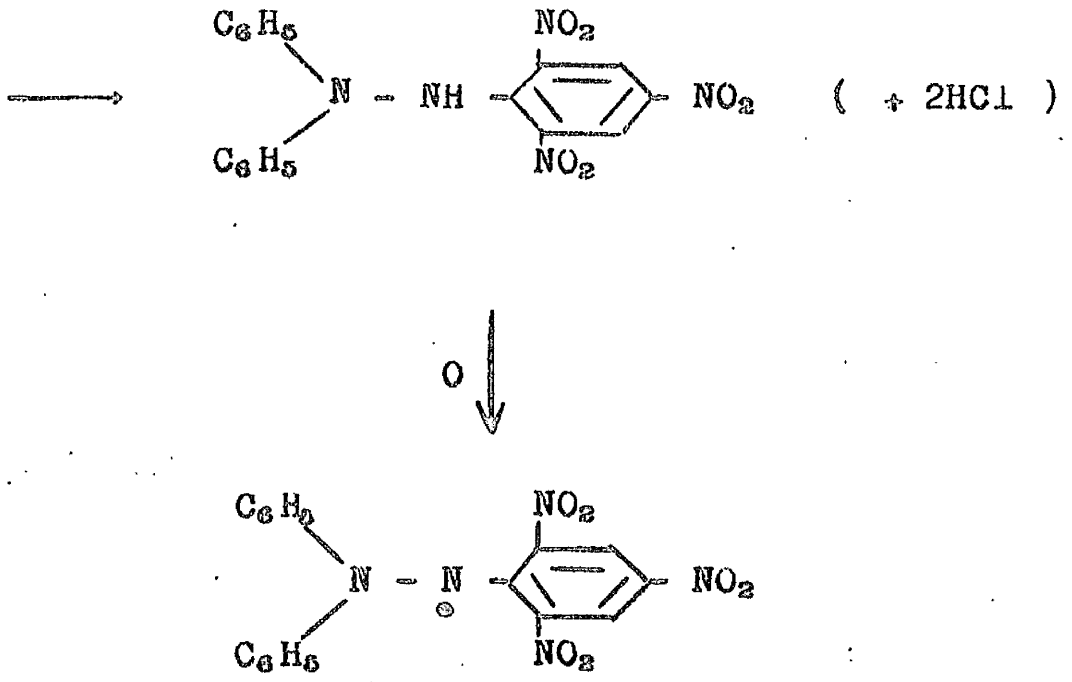
The filtrate was washed with two 115 cc portions of water and was then concentrated to 70 cc on a steam bath, and diluted with 70 cc of warm absolute ethanol.

On standing overnight brick red prism - like crystals formed. This was 1:1' diphenyl-2-picryl hydrazine.

5.1 gm of this compound, 5.1 gm anhydrous sodium sulphate, and 31.4 gm lead dioxide were shaken in 100 cc of distilled analar benzene for two hours. The solid residue was filtered off and the filtrate evaporated to dryness at room temperature on the vacuum line. Violet crystals formed and these were recrystallised twice from a 2:1 benzene:ligroin mixture.

Equations:-





(DPPH.)

Solvents. Analar acetone was used for calibrating reaction vessels.

Analar benzene was used for osmotic pressure and viscosity measurements.

Anaesthetic grade chloroform was distilled immediately before use, and all solutions prepared from this were stored in darkness.

Apparatus.

High vacuum line (1). This consisted of a series of traps and vacuum tested taps of 4 - 6 mm bore in pyrex glass connected to the pumping system which was

a mercury diffusion pump backed by a rotory oil pump. All taps were greased with Apiezon grease, M or L high vacuum grade. Cold traps were placed immediately before and after the mercury diffusion pump and a solid carbon dioxide (Drikold)/ acetone mixture was used as coolant. Using this system a vacuum of at least 10^{-4} mm Hg. could be obtained. All reaction vessels were tested with a Tesla coil to make sure that there were no pin - hole leaks in the vessels.

High vacuum line (2). This was similar to the first vacuum line, but had an inlet point after the mercury diffusion pump to allow carbon dioxide to be distilled in from the condensing coil of the gas purification train. Cold traps, cooled as before, were provided for storing the carbon dioxide and other reactants as required. An outlet point was provided for filling the geiger - tube, and a manometer constructed of 2.5 mm capillary tubing was used to measure pressures.

High vacuum line (2) was used only for handling active carbon dioxide.

Reaction vessels. All reactions were carried out in vacuum tested pyrex glass vessels.

Simple dilatometers. These were used for inhibition measurements. Dimensions are shown in Fig.(1)

Modified dilatometers. These vessels were used for the preparation of radioactive polymer samples. They had a flattened bulb so that the optical path length was short. Thus higher initiator concentrations could be used. A typical vessel is shown in Fig.(1)

All dilatometers were constructed from 1.5 mm Veridia tubing.

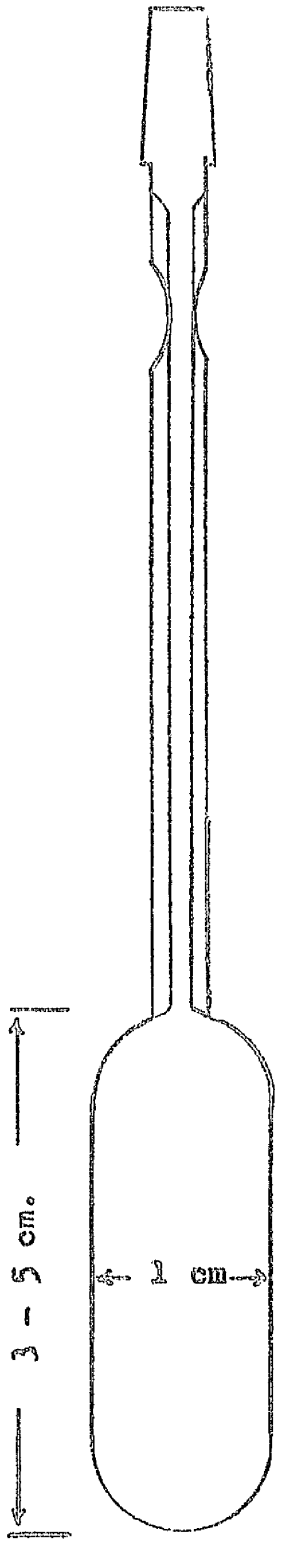
Absorption cells. Cells as supplied by the Cambridge Instrument Co. were modified so that they could be attached to the vacuum line. All cells were optically matched before use by moving the position of the locating collar.

Cathetometer. The cathetometer used could be read to 0.001 cm.

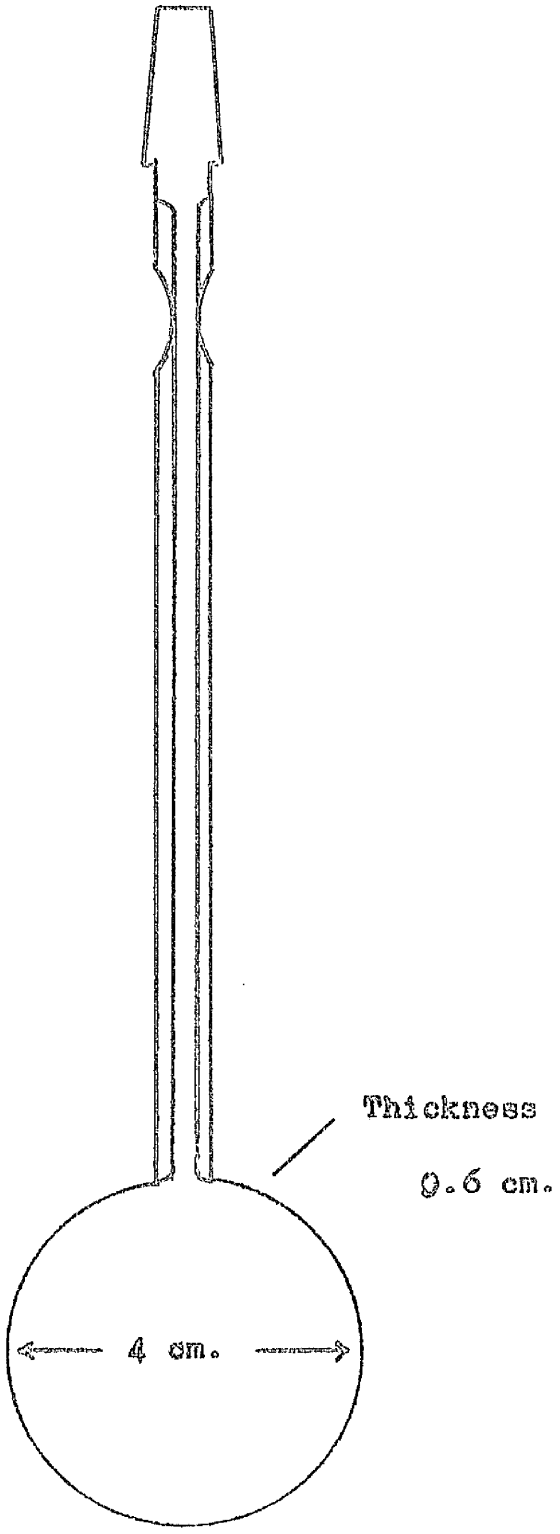
Absorptiometer. A Unicam type SP 1400 prism absorptiometer was used. This has an effective wavelength range of 4,000Å to 7,000Å and rapid colorimetric or absorptiometric estimation of samples can be made. The unit was operated from a 12 volt constant voltage transformer.

Thermostatically controlled water bath. This consisted of a 25 litre cylindrical pyrex glass tank.

Dilatometers. Fig. (1)



(Simple)



(Modified)

It was lagged with a one inch thick layer of fibre glass and surrounded by an aluminium jacket. Windows for observation and irradiation were left clear. A 60 watt 12" tubular single cap lamp was used as the heat source, this being controlled by a mercury - toluene thermoregulator and a relay unit. Efficient stirring was provided by a propeller type stirrer. The normal operating temperature was 25 ± 0.02°C.

Irradiation. The source of irradiation was an Osira 125 watt medium pressure mercury vapour lamp. This was mounted in an asbestos - cement box and was operated in conjunction with a choke and capacitance. The light emitted was passed through a Chance OX1 filter giving light mainly of wavelength = 3650Å.

Osmometer. A Pinner - Stabin osmometer[40] was obtained from Polymer Consultants Ltd. The osmometer is constructed throughout in borosilicate glass and stainless steel and the joints are made with Teflon gaskets. The cell volume is about 3.4 cc and the effective membrane area is 9 sq.cm so that static equilibrium is reached fairly quickly.

Additional equipment required for radiotracer work.

Micro-combustion furnace. A standard micro - combustion furnace of the type described by Pregl & Grant[41] was used. The combustion tube was made from fused quartz

and the samples of polymer to be oxidised were placed in small platinum boats.

Geiger - Muller tube. A Geiger - Muller tube, type no. GA 10M , as supplied by Twentieth Century Electronics Ltd. was used. This tube was ideally suited for gas counting using samples of low activity.

Stabilised power unit, type no. N103. This unit, supplied by Dynatron Radio, is designed to give a stable source of high voltage free from ripples and pulses for use with Geiger - Muller tubes. The unit, operating from the mains supply, produces a variable stabilised voltage of from 300 to 3,300 volts at a positive or negative potential with respect to the chassis. The accuracy of the output voltage is quoted as $\pm$1% on any voltage setting for both positive and negative polarities.

Scaler type no. 1009E. This was also obtained from Dynatron Radio. The function of this unit is to count random or regular electrical impulses the amplitude of which is greater than a predetermined value, which may be between +5 and +50 volts. The electrical impulses to be counted can be fed directly to the normal input circuit, or derived from a Probe unit such as Probe unit type no. 110A. The pulses are applied to

the discriminator. The discriminator bias may be set at any value between +5 and +50 volts so that pulses below this predetermined value can be effectively rejected. The paralysis time can be preset in steps over a range extending from 5 to 10,000 micro - seconds. This circuit causes the scaler to become ineffective for the preset period immediately after it has been triggered by a pulse. This facility is used to avoid the spurious discharges which can occur in a Geiger - Muller tube.

The scaling unit was operated in conjunction with a cooling unit type 1172C to ensure a minimum temperature increase within the scaler.

Timing unit, type no.N108A. This unit, also supplied by Dynatron Radio, is used to switch off the scaler either at a preset time or after a preset number of counts have been recorded. The unit has a maximum time store of 99,999 seconds and a maximum count store of 999,999 counts.

Probe unit, type no. 110A. This unit, supplied by Ericsson Telephones Ltd., is designed to minimise counting errors which are liable to occur in a Geiger - Muller tube. The main sources of error are spurious pulses which may arise in the tube and the unknown dead time of the tube.

Both of these errors can be eliminated by the use

of the Probe unit the counting of spurious pulses is prevented by the reduction in voltage brought about by the quench pulse, and the dead time is replaced by the quench pulse.

Procedure.

All polymerisation reactions and measurements of inhibition periods were carried out under high vacuum conditions. In photochemical initiation it is desirable that the intensity of irradiation should be uniform, otherwise the rate of initiation will vary throughout the vessel. To ensure uniform illumination, the light transmitted from the solution should be a large fraction of the light incident on the system, i.e. only a small amount of the light energy should be absorbed in passing through the system.

The amount of light absorbed in any photochemical polymerisation is a function of the concentration of the initiator (c) and the light path through the solution (l). The extinction coefficient of the initiator (e) is also involved. Beer's Law relates the intensities of incident light, (i) and transmitted light (i_o), thus:-

$$i = i_o . 10^{-e.c.l.} \qquad \ldots(2.1)$$

If it is decided that not more than 20% of the incident radiation is absorbed, then the maximum

permissible initiator concentration can be calculated for any particular size of reaction vessel.

Calibration of dilatometers.

The dilatometers were thoroughly cleaned in water and rinsed in analar acetone. The volume of the bulb was found by adding analar acetone from a burette. The capillary stem was constructed from 1.5 mm Veridia tubing.

One centimetre length of the capillary stem was expressed as a volume percentage of the bulb, and since the percentage polymerisation is related to the percentage contraction, the rate of fall of the meniscus could be directly related to the rate of reaction in terms of % polymerisation/ unit time.

The relationship used between % contraction and % reaction was given by Schulz & Harborth[42] as:

23.06% contraction = 100% polymerisation.

Filling of dilatometers.

The initiator and inhibitor were introduced into the reaction vessel in the form of standard chloroform solutions. The dilatometer was connected to the vacuum line and the solvent distilled off. Methyl methacrylate was distilled into the dilatometer from the storage flask on the vacuum line. The

dilatometer was then sealed off at the constriction with a hand torch.

Filled dilatometers were stored in an acetone/drikold mixture until ready for use.

Measurement of the rate of removal of DPPH.

1) Inhibition period measurements. The filled dilatometer was completely immersed in the water bath and about 15 minutes allowed for the reactants to reach thermal equilibrium. A cathetometer was focussed on the meniscus in the capillary stem and irradiation commenced. The rate of fall of the meniscus was observed and a graph of %polymerisation versus time was drawn. The intercept on the time axis was taken as the inhibition period. As can be seen from Fig.(6) this corresponds fairly closely with the time when polymerisation is first detected.

2) Absorption measurements. The cells were optically matched at 5240Å using the SP 1400 prism absorptiometer and then filled as described. The initial optical density was recorded and the cell was placed in the water bath. The cell was removed at regular intervals and the optical density of the solution measured. A graph of optical density against time was drawn and the rate of removal of DPPH. calculated.

Measurement of the rate of polymerisation in the radiotracer experiments.

Active AIBN. was carefully added to the dilatometer in the form of a chloroform solution in the usual manner. The solvent was removed on the vacuum line and the required amount of methyl methacrylate distilled into the dilatometer. The polymerisations were stopped after 5 - 8% reaction, and the polymer precipitated immediately.

Precipitation of polymer.

The contents of the dilatometer were transferred to a small beaker and a similar volume of benzene added. This solution was slowly added to a large excess of methanol, vigorous stirring being used. The polymer was obtained in a finely divided form and was filtered off and dissolved in a small volume of benzene. The polymer was reprecipitated twice and the final polymer obtained was freeze - dried from a dilute solution of polymer in benzene, thus giving the polymer in a form which was readily soluble (for molecular weight measurements) and also very suitable for combustion.

Molecular weight measurement.

Percel 600 gel cellophane membranes were used. These were supplied by Polymer Consultants Ltd. in

50% aqueous acetone.

A series of acetone/water solutions was prepared and the membranes immersed in each solution for several hours. The membranes were then transferred to anhydrous acetone, and a series of acetone/benzene solutions up to pure benzene was prepared. The menbranes were immersed in each of these solutions in turn for 24 hours. Finally the menbranes were transferred to pure benzene and stored until required for use.

A pair of membranes was fitted to the osmotic cell using the Teflon gaskets and the stainless steel flanges. The cell was filled with benzene and put in its outer jacket in the water bath. Sufficient benzene was added to the jacket to ensure that the cell and the reference limbs were immersed. A cathetometer was focussed on the two capillary stems, and the cell left to come to equilibrium. Only if there was no difference in the two capillary levels was the pair of membranes selected.

The osmotic pressure of a series of dilute polymer solutions was measured and extrapolated to infinite dilution. The membranes were checked to ensure that there was no cell constant from time to time by using pure benzene as above.

Handling of the osmometer.

Membranes were handled carefully using flat tongs and were kept immersed in benzene while being fitted to the stainless steet flanges. Air bubbles between the membrane and the flange were expelled by gently pressing the membrane against the flange while still under benzene. The flanges were tightly but evenly bolted together and it was found that the bolts could be tightened further after the osmometer had been immersed in benzene for some hours. The bolts were again tightened until they could be turned no further and it was found that the bolts now remained tight.

When a suitable pair of membranes had been selected, great care was taken to ensure that the osmometer was thoroughly rinsed with benzene after each osmotic pressure measurement. The osmometer was filled and emptied using a syringe with a 10" needle and the osmotic pressure of the solution of lowest concentrated solution was always measured first, followed by solutions of increasing concentration. The benzene in the solvent bath was changed for each difierent polymer sample, and the cell checked to ensure that there was no cell constant.

Dilute polymer samples were always added to

the osmotic cell at the temperature of the water bath, the capillary measuring limb being filled to a position below the reference limb. The solution rose to a steady maximum height in 3 - 4 hours. A similar result could be obtained by filling the cell so that the level in the measuring limb was well above the reference level, and allowing the liquid to fall to its equilibrium value over a longer period. In the absence of diffusion of low molecular weight polymer through the membrane the result obtained by either method is the same.

Oxidation of polymer.

A platinum boat was filled with polymer and placed in the quartz combustion tube. A steady stream of oxygen, free from carbon dioxide, was passed through the tube. The polymer was heated slowly with the travelling furnace and the vapours passed through a bed of copper oxide in the tube which was heated to 850^{o}C. Most of the oxidation occurred here. Particular care was needed when heating the polymer to avoid an explosion which could occur if the polymer were vaporized too quickly by the travelling furnace.

The products of combustion were water vapour, oxides of nitrogen, carbon dioxide, and excess

oxygen. The oxides of nitrogen were removed by passing the gases through a bed of lead dioxide heated at 180°C. Water vapour was removed by passing the gases through a U - tube filled with magnesium perchlorate (anhydrone). The remaining gases were passed through a spiral coil which was cooled in liquid oxygen, and was open to the atmosphere at one end. The carbon dioxide condensed in the coil. When all the carbon dioxide had been collected, the coil was isolated from the furnace, closed to atmosphere, and opened to the vacuum system. The carbon dioxide was degassed thoroughly, slowly at first, and then allowed to diffuse into a receiving trap on the vacuum line. This trap was then closed to the vacuum line and kept surrounded by liquid oxygen. Some carbon disulphide was placed in another trap and thoroughly degassed.

The Geiger - Muller tube was attached to the line and evacuated. A cathetometer was focussed on the mercury meniscus in the manometer, and by careful manipulation of taps a pressure of 6.00 cm of carbon dioxide was admitted to the tube. No difficulty was encountered in measuring the pressure to within 0.001 cm by using the cathetometer, and 6.00 cm could always be obtained by recondensing any excess back into the receiving trap.

In practice the carbon dioxide was allowed to vaporize through the line and recondense in the receiving trap several times to ensure thorough mixing of the gases before any attempt was made to fill the tube. For the reason given below 3.00 cm of carbon disulphide vapour was admitted to the tube after the carbon dioxide had been added. It was more difficult to control the addition of the carbon disulphide vapour and once added no further adjustment could be made.

Carbon dioxide alone is a poor counting gas and its behaviour is not improved bynthe addition of the usual quenching vapours such as alcohol or xylene. However, it has been found that the addition of carbon disulphide vapour produces a mixture with good counting characteristics.[43,44]

Counting procedure.

All counting was done in a room reserved for this purpose. The tube was connected to the Probe unit and the minimum voltage required to cause discharge was found. This value is termed the threshold voltage. The plateau region was then established. As will be made clear later, it is necessary to count for a fair period of time since the discharges occur in a random manner. Short counts can give very misleading results.

Background activity.

In order to interpret the results obtained with varying amounts of AIBN. it is necessary to know the background activity. This was measured by oxidising a sample of inactive polymer and counting in the usual manner. The background count was measured from time to time and was found to be constant within the limits of experimental accuracy.

The background activity is due to the activity associated with the materials of construction of the Geiger - Muller tube, the penetration of ionising radiations through the walls of the tube, and the natural activity of the polymer. The background activity should be subtracted from the activity obtained with active polymer samples to find the true activtiy due to the presence of AIBN. fragments in the polymer.

C H A P T E R 3.

RESULTS.

Before considering the results obtained by the various methods of measuring the rate of initiation, it is essential to establish that the monomer used does obey the kinetic analysis given on pages 4 - 6, since any significant deviation from this scheme will complicate the interpretation of the results obtained.

The rate of polymerisation is given by:

$$-d[M]/dt = K_p/(K_t^{0.5})\ I^{0.5}[M] \qquad \ldots(1.10)$$

and it can be seen that the reaction rate varies as $I^{0.5}$ in a sensitised polymerisation at a fixed temperature. The rate of initiation, I, is dependent on the rate of decomposition of the initiator, which in turn, is governed by the initiator concentration and the intensity of irradiation. In this work the intensity of irradiation has been kept constant, and the only experimental variable is therefore the initiator concentration.

Fig.(2) shows a plot of rate of polymerisation against $[AIBN]^{0.5}$. This is linear, indicating that the rate of polymerisation is proportional to the square root of the initiator concentration, and since the line passes through the origin, there is no appreciable dark reaction under the conditions of study, i.e., thermal decomposition of the initiator to give radicals which can initiate polymerisation does not occur to any extent. The log. Rate - log.AIBN. plot shown in Fig.(13) is also instructive, again showing the dependence of the reaction rate on the initiator concentration. (Fig.(13) follows page 64.)

The number average degree of polymerisation, $\overline{DP}_n$, is usually influenced by the addition of foreign substances to the polymerising medium. The $\overline{DP}_n$ is related to the rate of polymerisation thus:-

$$1/\overline{DP}_n = K_{tr}/K_p + R_p.K_t/K_p^2.M^2 \quad ...(3.1)$$

where K_{tr} represents the transfer constant for chain transfer between a molecule of monomer and a growing polymer radical. A graph of $1/\overline{DP}_n$ A graph of $1/\overline{DP}_n$ against R_p therefore pass through the origin only if K_{tr} is zero, or if the ratio K_{tr}/K_p is very small.

A graph of $1/\overline{DP}_n$ against K_{tr}/K_p is very small. polymers prepared is given in Fig.(3). This plot is linear and there is a negligible intercept on the vertical

Graph of rate against $\sqrt{AIBN}$

Fig.(2)

$10^4/D_{12}^0$
0
1
2
3
4
5
6
5
10
15
20

axis, so that K_{tr} must be exceedingly small, and it can therefore be said that the end groups in the polymer chains formed have all been derived from the initiator or as a result of a disproportionation reaction between two growing polymer radicals.

It can be concluded therefore on the basis of the foregoing relationships that methyl methacrylate does conform to the kinetic scheme set out in pages 4 - 6.

In a photochemical polymerisation only those radiations which are absorbed by the reacting system are effective in promoting chemical reaction. As previously mentioned, it is desirable that the rate of reaction should be uniform and for this to be so it is necessary that only a small fraction of the radiation should be absorbed by the system.

By appling Beer's law it is possible to select experimental conditions such that not more than say 20% of the light is absorbed Beer's Law can be expressed:-

$$i = i_0 . 10^{-e.c.l.} \qquad \ldots(2.1)$$

and for AIBN. Overberger et al. [38] have given the value of e as 12 $mol.^{-1}l.cm.^{-1}$ at 3650Å. In the experiments involving DPPH. the optical path length of the cells was 1 cm. Assume that 20% of the light may be absorbed. By substituting these figures in

Beer's Law, the maximum concentration of initiator, c, which may be used is 8.1×10^{-3} mole.l.$^{-1}$

The actual concentrations of AIBN. used ranged from $1.22 - 4.88 \times 10^{-3}$ mole.l.$^{-1}$, so that again applying Beer's Law, the light absorption which occurred ranged from about 3% to 12% due to the presence of AIBN in the reaction mixture.

In the radiotracer work it was desired to use a greater range of concentrations, and accordingly, the length of the light path was reduced to 0.7 cm. Over the range of initiator concentration used, the light absorption varied from about 2% to 20%.

Absorption spectrum of DPPH.

The absorption spectrum of DPPH has been measured in analar acetone and distilled chloroform over the range 3600 - 6400 Å, as shown in Figs.(4) and (5). In chloroform the maximum absorption occurs at 5300Å and the extinction coefficient at this point is 26.5 gm.$^{-1}$l.cm.$^{-1}$. The molecular weight of the DPPH. prepared was 470, which comfirms the work of Lyons & Watson[26] who indicated that DPPH. forms a complex with the solvent from which it is recrystallised. The theoretical value for a 1;1 DPPH:benzene complex is 466. The extinction coefficient calculated for pure DPPH. from the above results is 32.1 gm.$^{-1}$l.cm.$^{-1}$

Absorption curve of DPPH. in acetone. Fig.(4)

Absorption curve for DPPH. in chloroform. Fig.(5)

which is in good agreement with the value of 32.2 $gm.^{-1}l.cm.^{-1}$ given by Lyons & Watson.

Direct observation of the inhibition period produced by the addition of DPPH.

Dilatometers, calibrated and filled as described, were placed in the water bath. The meniscus observed in the capillary stem and contraction readings noted after varying time intervals. The inhibition period was found by extrapolating the steady rate of polymerisation back to the time axis as shown in Fig.(6). This indicates that the inhibition periods obtained with different concentrations of DPPH., the concentration of AIBN. having been kept constant. It is seen that the inhibition period is fairly sharp and that only a small amount of polymerisation occurs towards the end of the inhibition period. The rate of polymerisation after the inhibition period is also identical with the rate of reaction in the absence of inhibitor, within the limits of experimental error.

Fig.(6) refers to an initiator concentration of 1.22×10^{-3} $mole.l.^{-1}$ in each reaction. The DPPH. concentration ranges from $2 - 6 \times 10^{-5}$ $mole.l.^{-1}$ A graph of inhibition period against DPPH. concentration is shown in Fig.(7). The plot is linear and passes through the origin thus showing that there is a

Inhibition periods.

Fig. 1

Inhibition periods with various amounts of DPPH.

Fig.(7)

direct proportionality between the measured inhibition period and the amount of DPPH. used. The slope of this graph gives the rate of removal of DPPH., which is taken as being equivalent to the rate of initiation.

The same procedure was also repeated for three other concentrations of initiator, 2.44, 3.66, and 4.88×10^{-3} mole.l.$^{-1}$, the rate of removal of DPPH. being calculated in each case. A graph of rate of removal of DPPH., $-d[DPPH]/dt$, against the initiator concentration, $[AIBN]$ was drawn. This is given in Fig.(7). A linear relationship is again obtained, and the line can be represented by the equation:-

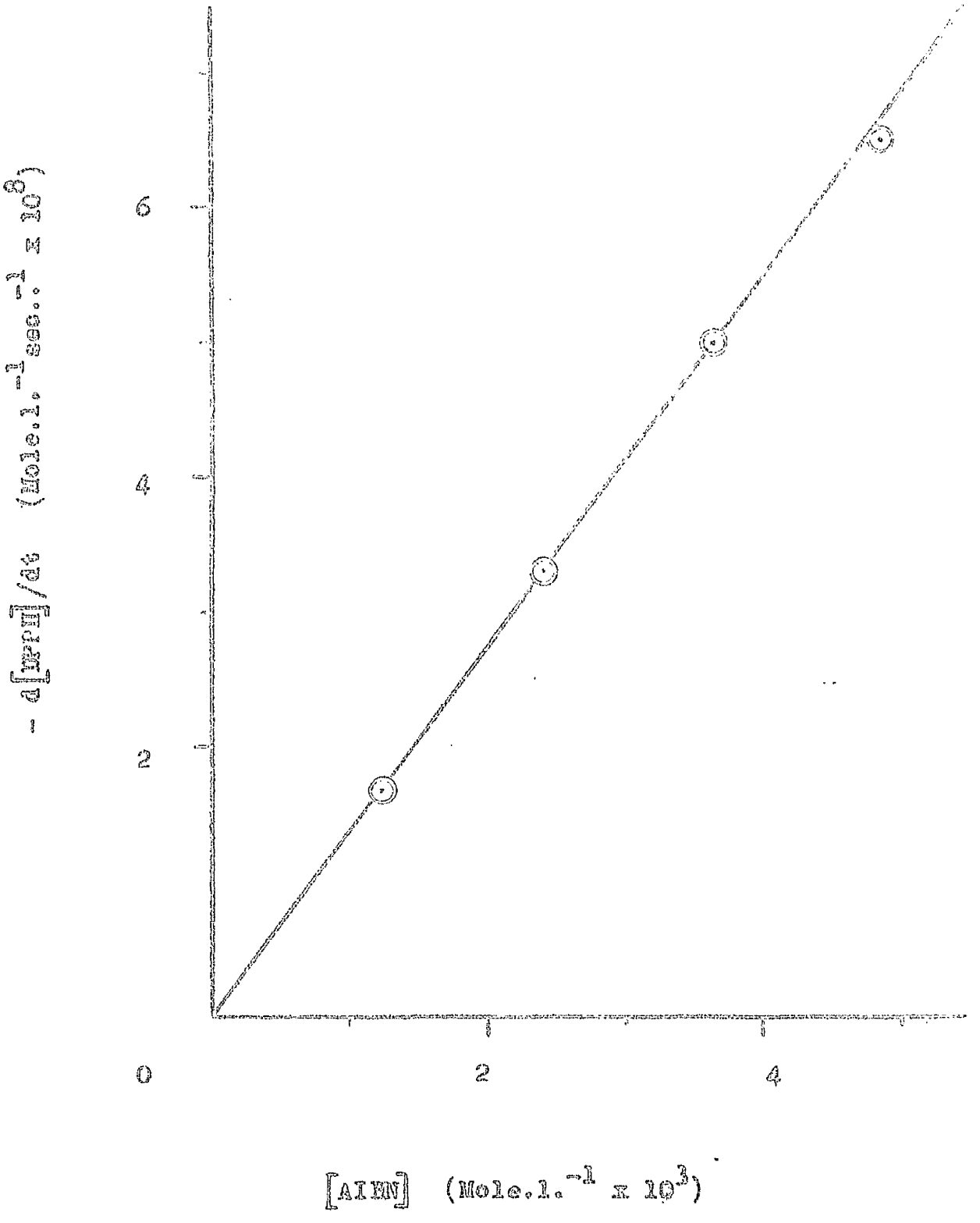
$$y = 1.36X \times 10^{-5}, \qquad \ldots(3.2)$$

where $X = [AIBN]$ in mole.l.$^{-1}$ and $y = -d[DPPH]/dt$ in mole.l.$^{-1}$sec.$^{-1}$

Determination of the rate of removal of DPPH. by spectrophotometric method.

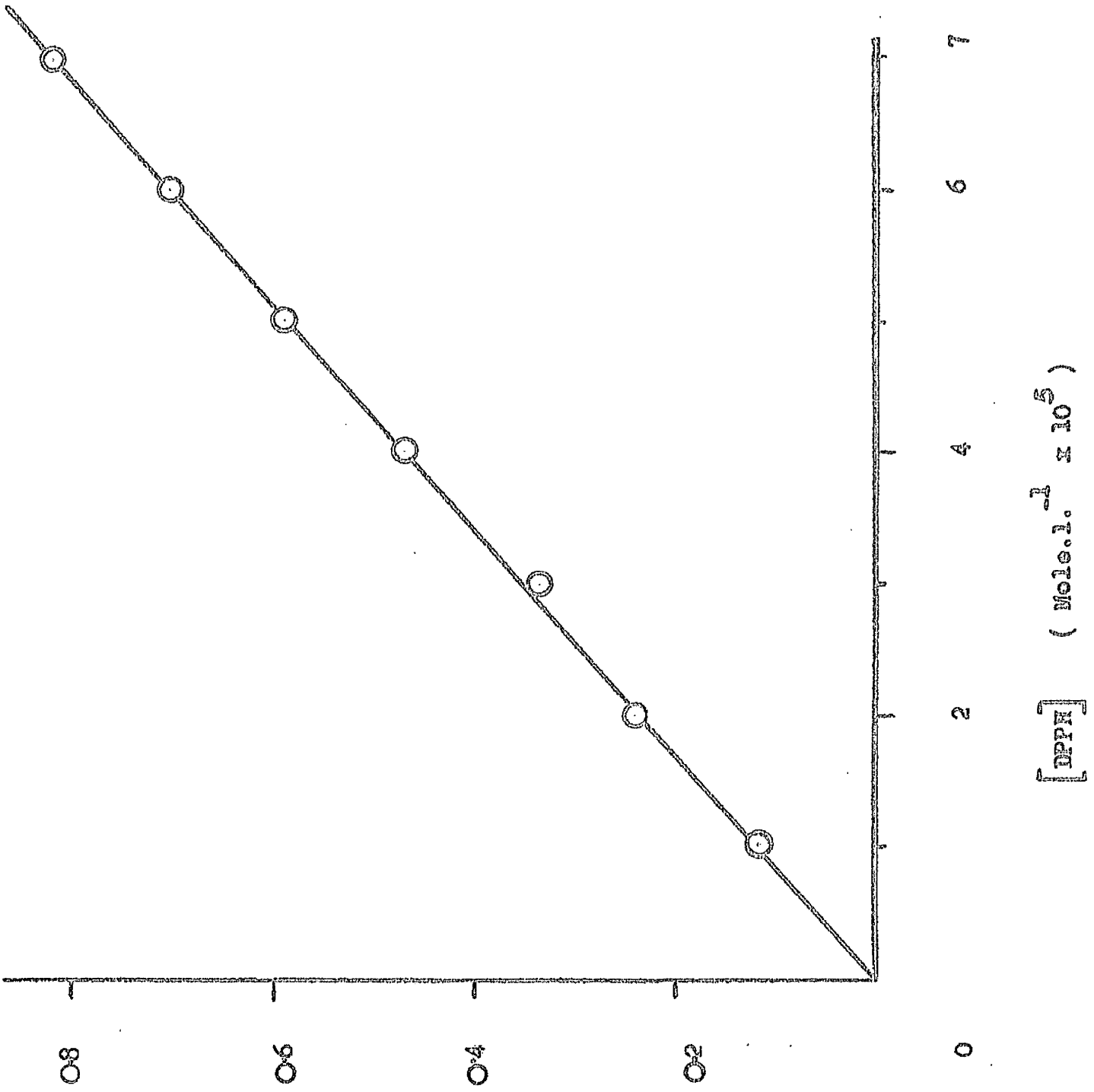
This method makes use of observations during the inhibition period. The rate of change of optical density is measured and can be related to the rate of change of DPPH. concentration since the initial optical density of any solution is proportional to the concentration of DPPH. added, as shown in Fig.(8). This is in agreement with Beer's Law. Thus, knowing the

Graph of $-d[DPPH]/dt$ — $[AIBN]$ Fig.(7a)



Relationship between optical density & DPPH concentration.

Fig.(8)



initial concentration of DPPH. present, and by plotting a graph of the optical density of the solution at various times, the rate of removal of DPPH. can be calculated. Fig.(9) gives a typical curve for an initiator concentration of 1.22×10^{-3} mole.l.$^{-1}$ and Fig.(10) shows the plot of $-d[DPPH]/dt$ against $[AIBN]$ for initiator concentrations of $1.22 - 4.88 \times 10^{-3}$ mole.l.$^{-1}$sec.$^{-1}$ The equation of this line is:-

$$y = 1.45X \times 10^{-5} \qquad \ldots(3.3)$$

A blank experiment was performed with methyl methacrylate and DPPH. only. When this was irradiated it was found that the rate of removal of DPPH. was negligible over a period equivalent to several times the usual induction period.

Determination of the rate of removal of DPPH. by using DPPH. as a radical scavenger in chloroform solution.

The spectrophotometric method of following the rate of removal of DPPH has been used to follow the reaction between DPPH. and AIBN. in a non - polymerising solvent, chloroform. Figs.(11) and (12) show a typical optical density - time curve and the $-d[DPPH]/dt$ against $[AIBN]$ relationship. It will

Optical density - time curve. Fig.(9)

Graph of $-d[DPPH]/dt = [AIBN]$

Fig.(10)

Optical density - time curve.

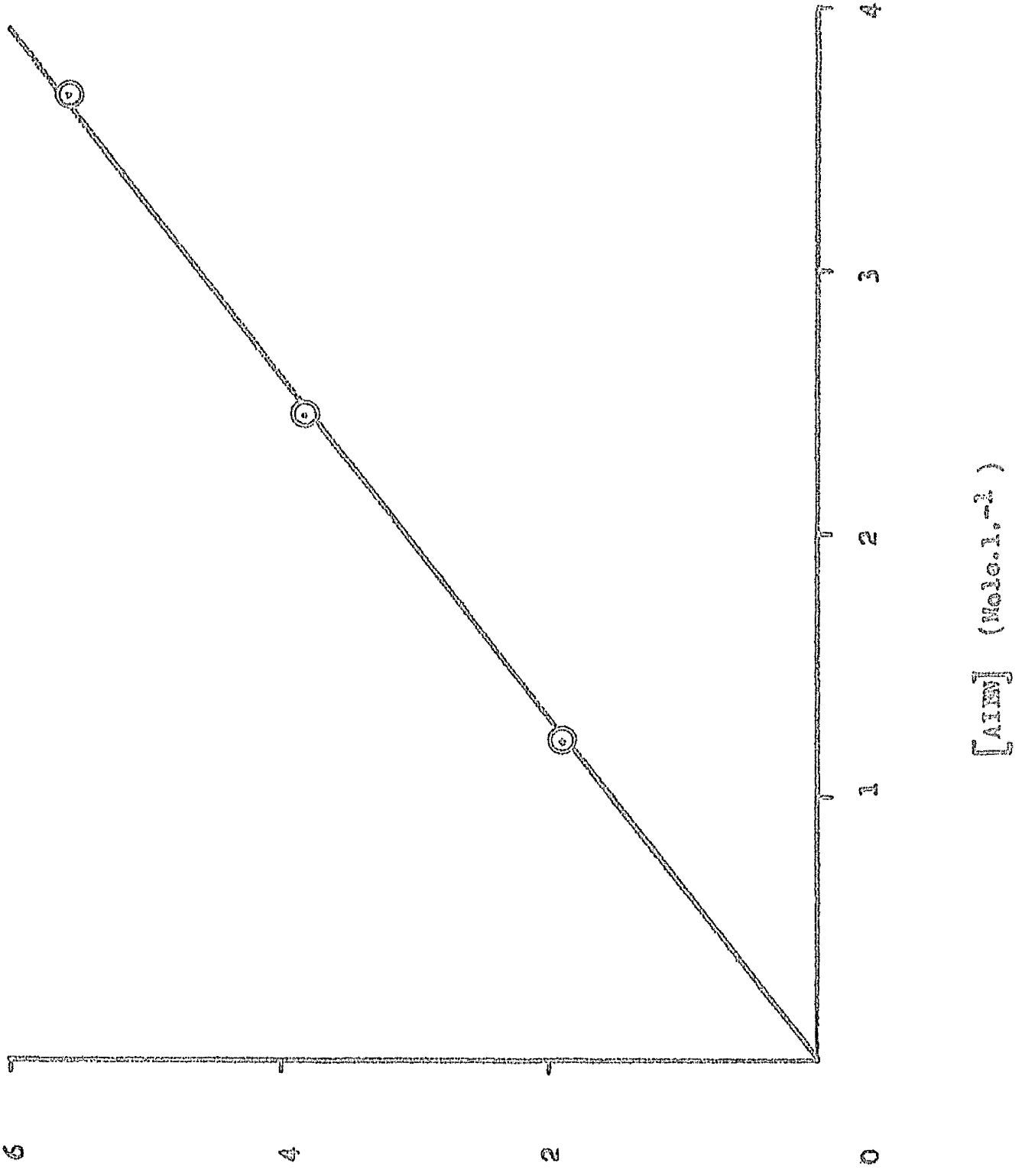
Fig.(11)

(Reaction in chloroform)

Graph of - d[DPPH]/dt against [AIBN]

Fig.(12)

(Reactions in chloroform)



be noted that the end point of the primary reaction period in chloroform is more clearly defined than in the presence of methyl methacrylate. The absorption of the end product in chloroform is also higher than in the case of the monomer. The relationship between $-d[DPPH]/dt$ and $[AIBN]$ may be represented:-

$$y = 1.55X \times 10^{-5} \qquad \ldots(3.4)$$

Table (1) summarises the results obtained by using DPPH to assess the rate of initiation.

Table (1).

[AIBN] Mole.$l.^{-1}$ x 10^{-3}	$DPPH_5$ Inhibition.	DPPH. Spectro.	DPPH. in chloroform.
1.22	1.67	1.79	1.90
2.44	3.31	3.53	3.8
3.66	5.0	5.3	5.55
4.88	6.5	7.1	-
	Units: Mole.$l.^{-1}$ $sec.^{-1}$ x 10^{8}		

Measurement of the rate of initiation from molecular weight and rate of polymerisation.

The molecular weight of the polymers prepared for the radiotracer work was measured. It is important that the method used to obtain the molecular weight is one which leads to the number average molecular weight. The number average molecular weight can be conveniently determined by measuring the osmotic pressure of the polymer in dilute solution.

The number average degree of polymerisation, $\overline{DP}_n$, can be found by dividing the number average molecular weight of the polymer by the molecular weight of the monomer. From a knowledge of the rate of polymerisation it is now possible to evaluate the rate of initiation by applying the equation:-

$$I = R_p / \overline{DP}_n \qquad \ldots.(1.40)$$

which holds for systems where termination is exclusively by disproportionation. This is the termination step which is now favoured in the polymerisation of methyl methacrylate, anf this has therefore been assumed in this work. If termination occurred exclusively by combination, it would be necessary to multiply the values derived for the rate of initiation by two.

Fig.(13) shows the log.rate against log.[AIBN]

Graph of log.(Rate) - log.[AIBN]

Fig.(13)

plot for these polymers. This has a slope of 0.49, thus indicating that the rate of polymerisation varies as $[AIBN]^{0.49}$. Further, chain transfer is unimportant in the polymerisation of methyl methacrylate, at least during the first 6% reaction, since there is virtually no intercept on the vertical axis, as shown in the $1/\overline{DP}_n$ against rate plot as given in Fig.(3)

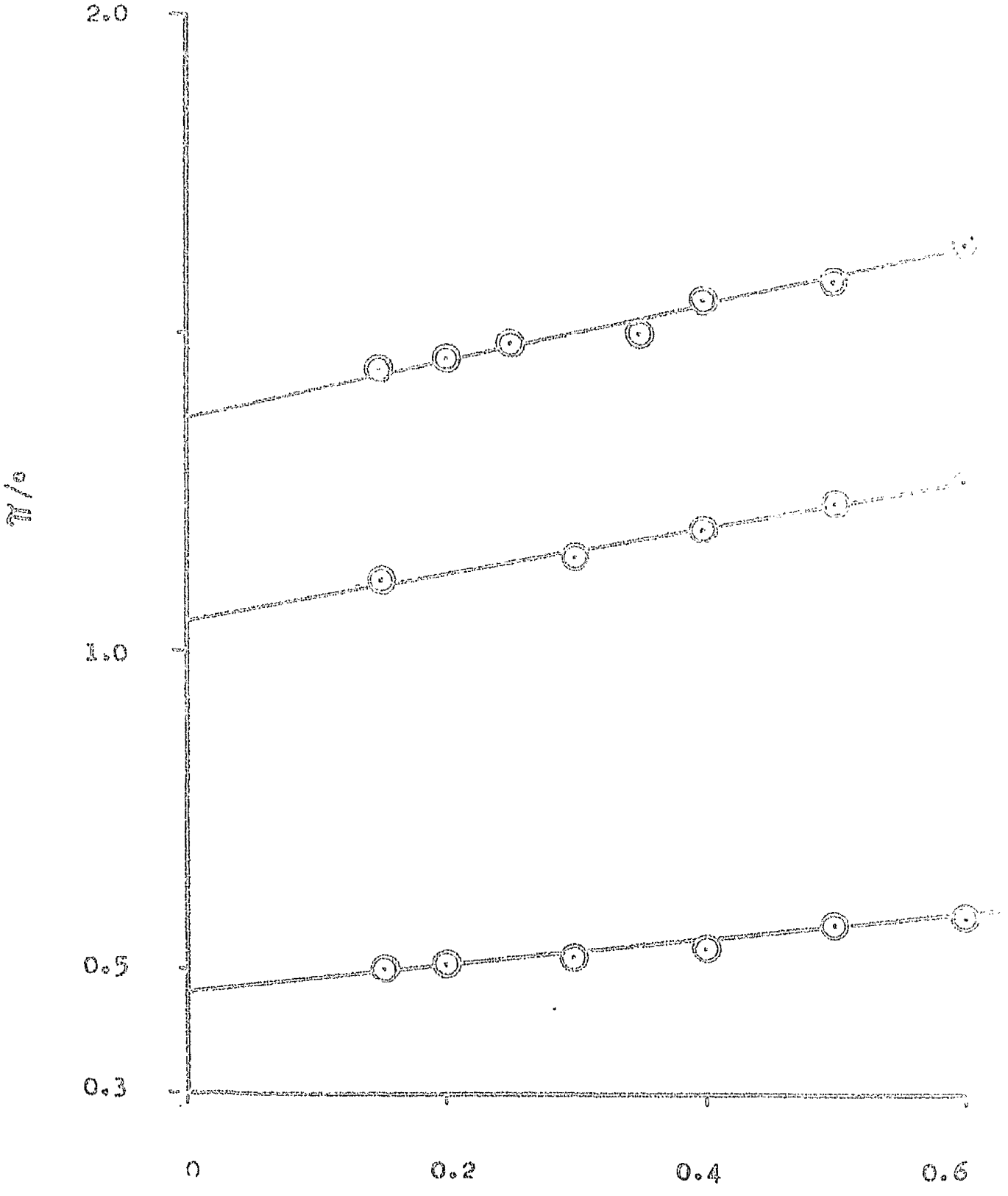
Table (2) summarizes the osmotic pressure data for these polymers, typical π/c curves being shown in Fig.(13a)

Table (2).

Osmotic pressure data for dilute polymer solutions In benzene at 18°C.

[AIBN]	1.22	4.88	7.32	9.76	12.2
c	π/c	π/c	π/c	π/c	π/c
0.15	0.496	0.872	1.130	1.248	1.441
0.20	0.503	0.884	-	1.269	1.453
0.30	0.512	0.909	1.142	1.304	1.479
0.35	-	-	-	-	1.500
0.40	0.526	0.933	1.189	1.342	1.548
0.50	0.564	0.959	1.226	1.381	1.578
0.60	0.577	0.985	1.259	1.419	1.638
(π/c)	0.461	0.832	1.048	1.185	1.370

c is in gm. polymer/100 cc benzene solution.


2.0
1.0
0.5
0.3
π/c
0
0.2
0.4
0.6
c (gm. polymer/100 cc. benzene)

In table (2) c is expressed in the units gm.polymer/100 cc. benzene solution and η is in cm. benzene solution.

Table (3) shows the calculated values of the rate of initiation and Fig.(14) shows the plot of log.I against log.[AIBN] The equation relating these variables is:-

$$y = 7.6x \times 10^{-6} \qquad \ldots(3.5)$$

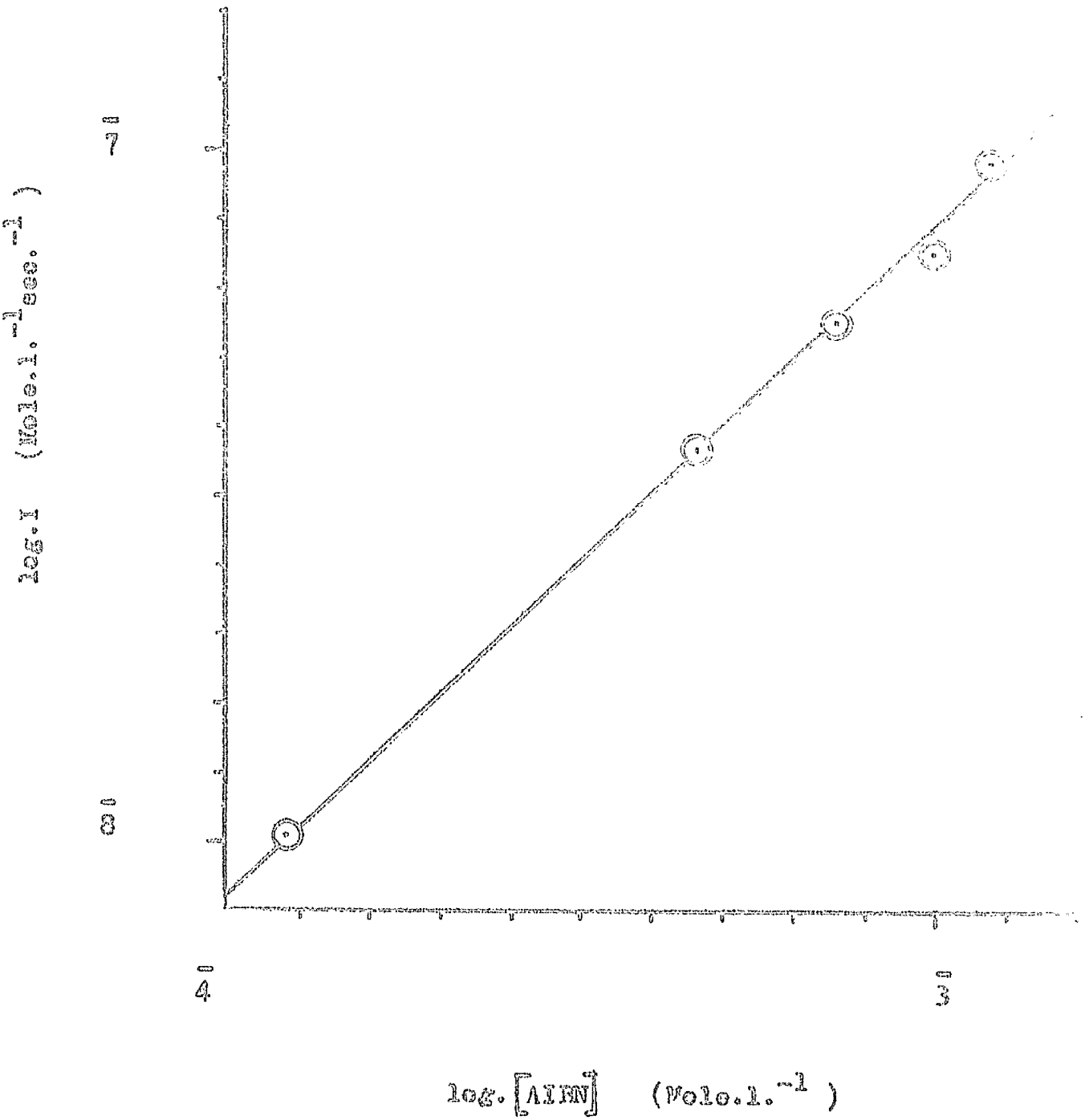
Table (3)

Rates of initiation by the molecular weight method.

[AIBN] $\times 10^3$	M.wt.	$R_p \times 10^5$	I $\times 10^8$
1.22	623,000	6.45	1.035
4.88	345,000	12.6	3.65
7.32	275,000	15.3	5.59
9.76	242,000	17.4	6.98
12.2	210,000	19.9	9.48

[AIBN] is expressed in mole.$l.^{-1}$ and R_p and I are expressed in mole.$l.^{-1}$ $sec.^{-1}$

Graph of log.I against log.[AlBN] Fig-(14)



Relationship between intrinsic viscosity and number average molecular weight.

The intrinsic viscosity of a dilute polymer weight of the polymer by the Houwink equation[45], which is expressed:- h

$\eta = K. \bar{M}_n^{\alpha}$, where η = intrinsic

$\eta = K. \bar{M}_n^{\alpha}$, where η = intrinsic viscosity and K and α are constants for the polymer - solvent system.

The intrinsic viscosity of each polymer was determined using an Ubbelohde viscometer modified so that the polymer solutions could be diluted in situ.

A graph of log.η against log.$\bar{M}_n$ was drawn, as shown in Fig.(15). This has the equation:-

$\log.\eta = \log.\bar{M}_n + \log.K$, and is of the form $y = mx + c$. The slope of the graph is thus equal to α and the intercept on the vertical axis corresponds to log.K

From the graph the following values were calculated:-

$\alpha = .73$

$K = 7.5 \times 10^{-5}$

log η
0.4
0.3
0.2
0.1
0
5.2
5.4
5.6
5.8
6.0
log M

Measurement of the rate of initiation by the radiotracer technique.

The physical measurements required for this method are the rate of polymerisation, and the relative activities of the initiator and the polymer, and the background radiation.

The rate of polymerisation was measured and the polymers were precipitated immediately thereafter. Three precipitations were employed since a trial activity measurement after, 1, 2, 3, 5 precipitations showed that there was no appreciable decrease in activity after 3 precipitations, i.e., all the uncombined initiator had been removed. Table (4) indicates the activity of the polymers after several precipitations.

Table (4)

Activity of polymers after several precipitations.

No. of pptns.	1	2	3	5
Activity. cpm.	127	120.2	120	119.9

The activity of the initiator was found by a dilution method, since it was felt undesirable to burn a sample of active initiator. Reasons for this

were:

a) the danger of an explosion when heating the AIBN. with the consequent release of a quantity of highly active gas;

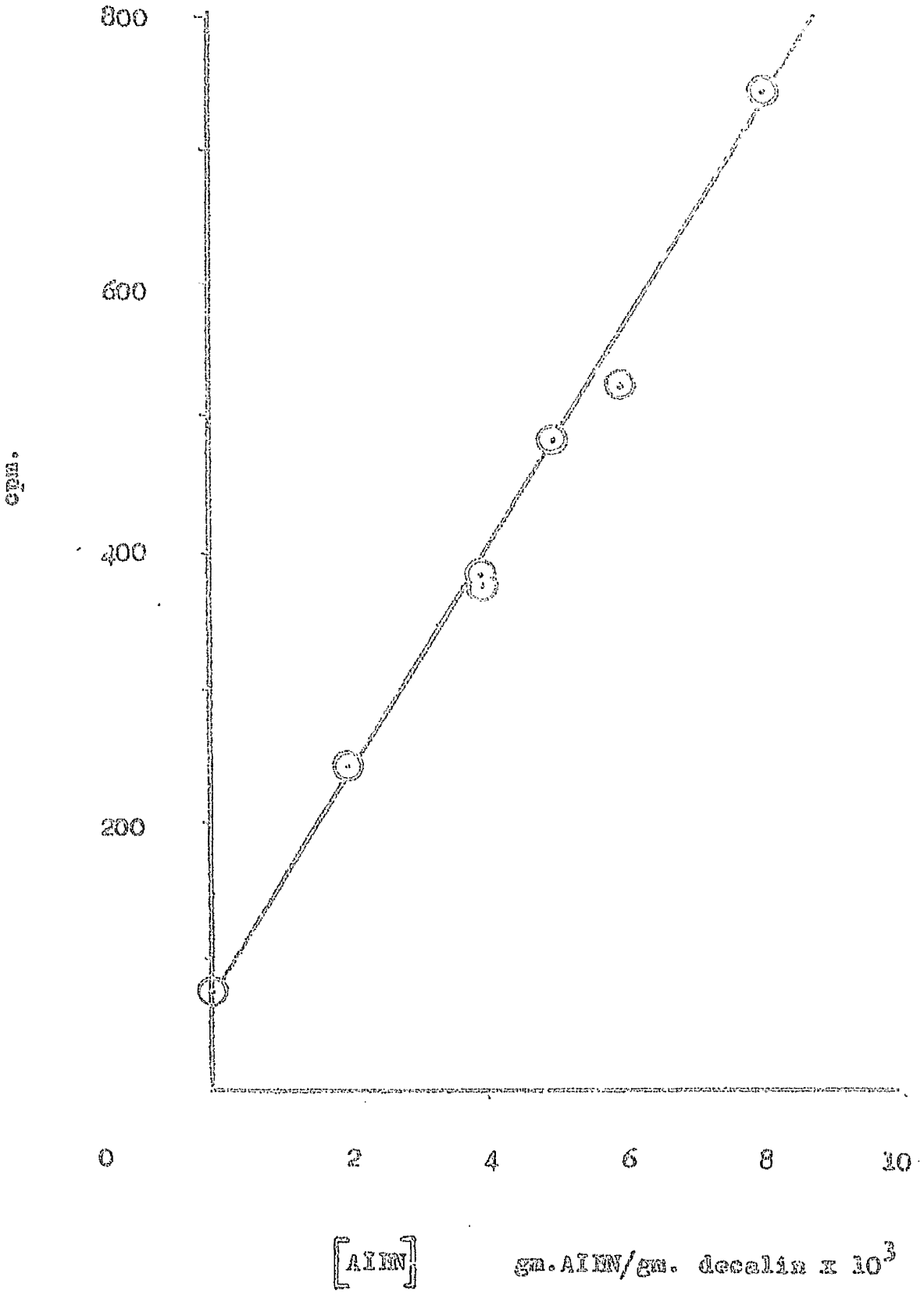
b) the possibility of accidentally allowing the gas to escape to the atmosphere; and

c) the desirability of obtaining a gas of similar activity to that from the polymers.

A series of solutions of active AIBN. in freshly distilled decalin was prepared and these were oxidised. It was important to ensure that complete combustion had been achieved and therefore the furnace was placed over the platinum boat for 30 minutes after all the liquid appeared to have vaporized. It was found that the combustion of the AIBN./decalin mixture could be easily controlled and there was therefore much less posibility of an explosion.

A graph of AIBN. concentration against activity in counts per minute is shown in Fig.(16) The activity of the AIBN. was calculated thus:

From this graph, for an AIBN. concentration of 5×10^{-3} gm AIBN./gm decalin, the observed count is 486 cpm. The background count is 72 cpm., so that the true count is 414 cpm.


800
600
400
200
cpm.
0
2
4
6
8
10
[AIBN]
gm. AIBN/gm. decalin x 10³

The sample contained:

$$\frac{5 \times 10^{-3} \text{ moles } {}^{*}C}{164} \quad + \quad \frac{1}{138} \text{ moles C}$$

(from AIBN.) (from decalin)

This gave:

$$\frac{8 \times (5 \times 10^{-3})}{164} \text{ moles } {}^{*}CO_2 \quad + \quad \frac{10 \times (1)}{138} \text{ moles } CO_2$$

i.e. 0.000244 moles ${}^{*}CO_2$ + 0.0725 moles CO_2.

Thus the fraction of ${}^{*}CO_2$ present is:

$$\frac{0.000244}{0.000244 + 0.0725} = \frac{0.000244}{0.072744}$$

For 100% AIBN., this fraction would be 1, and therefore:

$$\frac{\text{cpm. for pure AIBN}}{\text{(} {}^{*}C \text{ refers to carbon from active AIBN.)}} = 414 \times \frac{0.072744}{0.000244} = \underline{122{,}000 \text{ cpm.}}$$

A series of polymers ranging in AIBN. concentration of from 1.22 - 12.2 x 10^{-3} mole.l.$^{-1}$ was oxidised and the rates of initiation calculated using equation (1.44)

Table (5) gives the results derived for the rate of initiation by the radiotracer method. Typical counting curves showing applied voltage against cpm. are shown in fig. (16a)

Table (5).

Rates of initiation by the radiotracer method.

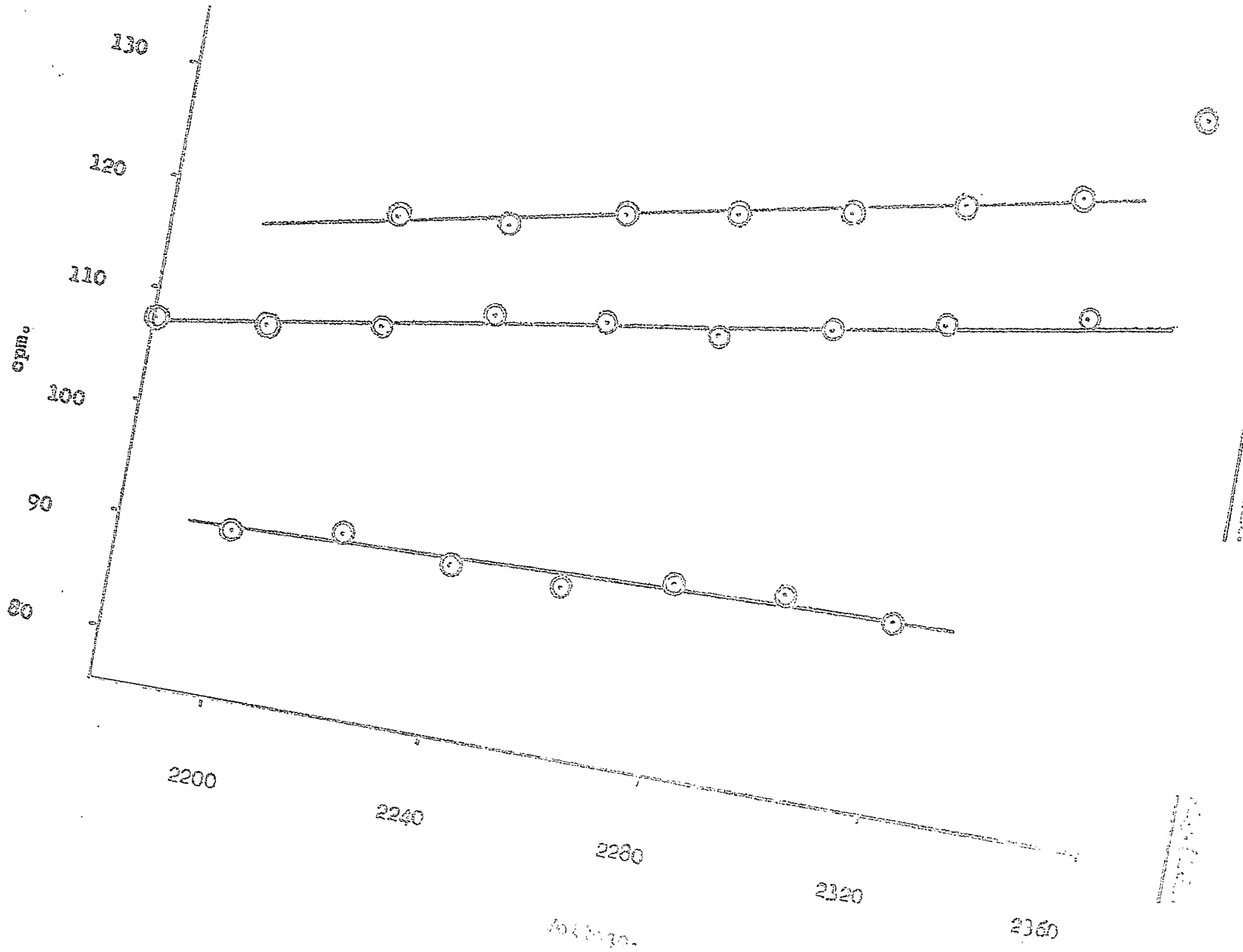
[AIBN] x 10^3	-d M/dt x 10^5	cpm.	I x 10^8
1.22	6.45	19	1.26
2.44	9.10	25	2.43
4.88	12.6	32	4.14
7.32	15.3	40	6.28
9.76	17.4	47	8.39
12.2	19.9	53	10.8

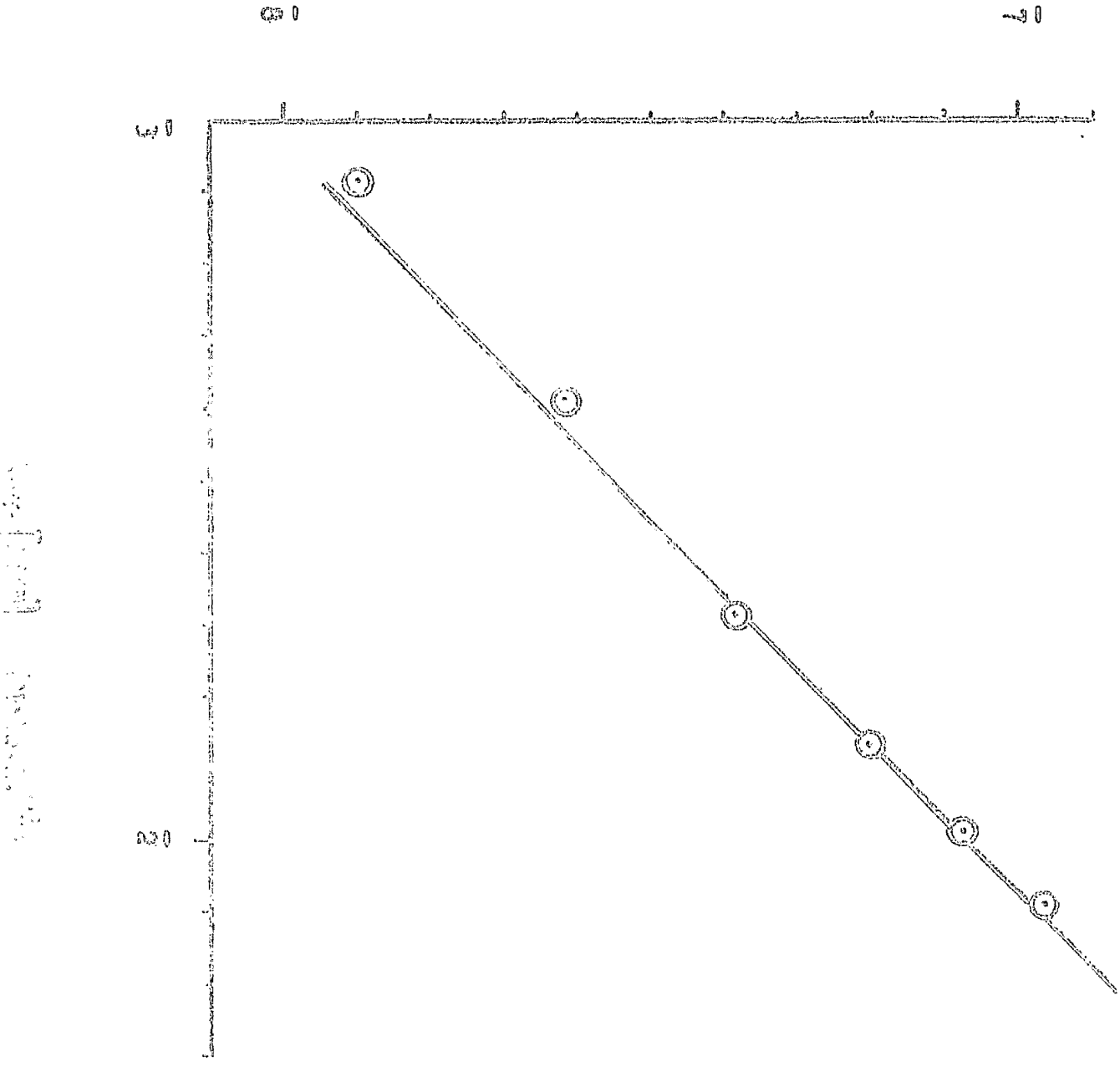
Units in moles, litres, and seconds.

The log.I against log.[AIBN.] plot is given on Fig.(17) and the equation relating I and [AIBN] is:-

$$y = 8.7X \times 10^{-6} \qquad \ldots(3.6)$$

From the above data, the kinetic chain length, ν, was evaluated from the relationship previously derived:


130
120
110
100
90
80
2200
2240
2280
2320
2360



Graph of log.I against log. [illegible]

$$\nu = 4/5 \times \text{Initiator activity/Polymer activity.} \quad \ldots(1.43)$$

The kinetic chain length and the number average degree of polymerisation are compared in table (6) and the number of initiator fragments per polymer molecule, $\underline{m}$, has been calculated.

Table (6).

Kinetic chain length and number average degree of Polymerisation.

[AIBN]	$\underline{\nu}$	$\overline{DP}_n$	$\underline{m}$
1.22	5140	6230	1.21
4.88	3043	3450	1.13
7.32	2439	2750	1.13
9.76	2078	2420	1.17
12.2	1840	2100	1.14

The average value of $\underline{m}$, the number of initiator fragments per polymer molecule is 1.15, thus showing that the predominant mode of termination in the polymerisation of methyl methacrylate is by disproportionation.

CHAPTER 4.

DISCUSSION.

It is important to realise the type and magnitude of error which is associated with the various methods which have been used to determine the rate of initiation.

Errors associated with DPPH.

DPPH. is a stable free radical but over a long period of time it might undergo decomposition due to exposure to light. The concentration of solutions prepared from this material would then be too low, and the apparent rate of initiation too high. If this decomposition did occur it should be indicated by a lower optical density for a standard solution, and the material could then be rejected.

There is the possibility of error in determining

the inhibition period by extrapolating the steady rate back to the time axis. This error will be more significant if the error is short. If there is a gradual change over an appreciable period of time before the steady rate is attained, i.e., if the inhibition period is not sharply defined, there may be a much greater error.

When irradiation was commenced a slight expansion of the reactants occurred over a period of between 30 seconds and 1.5 minutes. This was due to the exothermicity of the reaction and the expansion period was subtracted from the total inhibition period.

There may be a very slight error in the rate of removal of DPPH. as measured by spectrophotometry due to some decomposition of the AIBN. during the period that it is not exposed to the irradiation, i.e., while the optical density of the solutiom is being measured. This would result in the apparent rate of initiation being slightly high.

Molecular weight of high polymers.

All synthetic vinyl polymers consist of a large number of molecular species covering a broad range of sizes. The experimentally determined molecular weight should represent the average size of the various polymer chains. The nature of a polymerisation

reaction is such that at any instant the polymer molecules formed may vary in length from a few monomer units up to a molecule of very high molecular weight. Polymers prepared under normal conditions will thus consist of a wide range of different molecular species. This range of differing molecular species is termed the distribution of the polymer system, and is controlled by the reactivities of the reactants in the system.

A polymer is normally isolated from the monomer by precipitation. It is necessary that the molecular weight of the polymer recovered should be truely representitive of the agregate contributions of the various species present during the polymerisation reaction. This can only be so if the precipitation is essentially quantitative. To achieve this it is necessary to use a precipitant, or series of precipitants, which is effective over the entire molecular weight range. In particular, the low molecular weight species, which are more readily soluble, should be recovered.

In this work polymethyl methacrylate has been precipitated from benzene solution by methanol. Some calculations by Scanlan have been quoted by Ayrey & Moore[46]. It is shown that about 2% of the polymer molecules are lost if the number average molecular

weight of the recovered polymer is 2×10^5, and that losses are higher if the molecular weight is lower.

More recently, Fox et al. [47] have calculated that chains of $\overline{DP}_n$ less than 200 are soluble in methanol, and that the error due to this prefential solubility is between 3 and 10% for polymers of molecular weight between 650,000 and 200,000. They recommend precipitating polymethyl methacrylate by the addition of an acetone solution of the polymer to a 5 to 10 fold excess of Skellysolve B (a commercial mixture of low boiling paraffinic hydrocarbons). For this system, they estimate an error of from 1 to 4% over the above range.

In the determination of the rate of initiation by the radiotracer method, the loss of low polymer would mean that the observed activity of the polymer is too low, and thus the calculated rates of initiation would also be too low. On the other hand, if any uncombined initiator remains associated with the polymer, the error introduced may be much higher, and removal of all uncombined initiator is desirable, even at the expense of the loss of some low molecular weight polymer.

Bevington, Bradbury, and Burnett[36] have given a method of correcting for the loss of low molecular weight material. They give data for the determination

of the rate of initiation in a butyl acrylate - styrene system. They note an error of about 8% in the rate of initiation when the observed kinetic chain length is 80 and conclude that there will be very little error in the rate of initiation if the kinetic chain length is greater than 95, and the method of correction is applied.

Thus in a polymer of much higher molecular weight the error in the determination of the rate of initiation will be much less since the amount of low molecular weight material present will be a smaller fraction of the total range of species in the polymer.

Errors in determining the rate of polymerisation.

The relative error in determining the various rates of polymerisation should be small, and any deviations should be indicated on the rate - $\sqrt{\text{AIBN}}$. plot. There may however be error in converting dilatometric rate measurements to absolute rate units if there is any inaccuracy in the conversion relationship used. In the case of methyl methacrylate the relationship used is widely accepted.

Errors in measuring the activity of polymer samples.

Of the methods available for determining the activity of a polymer sample the technique of gas counting is the one which gives the most reliable

results, provided the conditions of counting are suitably chosen.

Errors in gas counting arise mainly because the discharge in the Geiger - Muller tube occurs in a random manner. In an activity determination of a sample of polymer whose activity is calculated to be 120 cpm., successive counts after one minute intervals might be say 93 cpm. and 140 cpm. It is clear therefore that very erroneous conclusions can be made from activity measurements which are made over a very short period. The reliability of results based on gas counting is dependent on the time of counting, and the ultimate accuracy can be made much greater than a count over a few minutes would indicate.

It is the usual practice in gas counting to choose a point on the plateau, e.g., the mid - point, and make the count at this point in every activity determination. In this work the procedure adopted was to make an activity determination at each of the points on the plateau and estimate the activity of the mid - point from a graph of applied voltage against cpm. Normally 4,000 counts were taken at each voltage. While it is possible to obtain a greater accuracy by taking 10,000 counts, at the mid - point, the method used here does have the advantage that there is less chance of error in the selection of the

mid - point of the plateau, and the number of counts considered in estimating the activity at the mid - point is in fact greater than 10,000.

Some idea of the error involved in counting can be seen in the following example. In a determination of the background activity at the mid - point of the plateau 5,000 counts were obtained in 69.5 minutes. Minute observations of the count were taken throughout the determination.

To analyse counting date at is helpful to apply statistical methods. Some definitions must be considered.

Consider a series of n determinations, $x_1, x_2, x_3 \ldots\ldots x_n$. Let the mean of these values be x. Then,

$$\text{Mean, } \bar{x}, = \frac{\Sigma x}{n} \qquad \ldots(4.1)$$

Variance, i.e., the scatter of results about the mean is defined as:-

$$\text{Variance, } V, = \frac{(x_1 - x)^2 + (x_2 - x)^2 + \ldots (x_n - x)^2}{n} \qquad \ldots(4.2)$$

and it can be shown that:-

$$V = \frac{\Sigma x^2}{n} - \bar{x}^2 \qquad \ldots(4.3)$$

Standard deviation, σ, is defined as:-

$$\sigma = \sqrt{V} \qquad \ldots(4.4)$$

Standard error of the mean, E, is defined as:-

$$E = \frac{\sigma}{n} \qquad \ldots(4.5)$$

The standard error of the mean was calculated for the above activity measurement and found to be 1.30 for 69 measurements. Associated with these results there is a probability, p, such that any value x, will lie between $\bar{x}$ + 1.30 and $\bar{x}$ - 1.30.

The mean of these 69 results is 72 cpm. From statistical tables it can be found that p is equivalent to 0.81, i.e., 81% of all the results will lie within the range 72 $\pm$ 1.30 and 19% of the results will have standard errors greater than 1.30

As the length of the counting period is increased n also increases and hence the standard error is decreased. Provided therefore that the loss of polymer during precipitation is negligible, and that activity measurements are made over a sufficiently long period, the error in the rate of initiation will be small, and will certainly be smaller than the error inherent in other methods.

It has been established that the monomer used in this work does follow the usual kinetic scheme for the polymerisation of a vinyl monomer, since the rate of polymerisation is $\propto$ to $[AIBN]^{0.5}$ and chain transfer

has been shown to be unimportant. (Figs. (2) & (3))

Figs. (4) & (5) showing the absorption curves for DPPH. in acetone and chloroform are in good a agreement with the curves given by Lyons & Watson[26] for a DPPH:benzene complex. Further the extinction coefficient calculated fron this data for pure DPPH. agrees well with the value found by Lyons and Watson. Molecular weight determination gave a value of 470 thus affording further evidence that DPPH as prepared by the method described in this work yields a complex containing the solvent from which it is crystallised. The theoretical value of molecular weight for a 1:1 DPPH.benzene complex is 466.

Fig.(8) shows a plot of optical density against DPPH. concentration. This is linear and passes through the origin, thus indicating that Beer's Law applies to the system.

Fig.(6) shows the effect of adding varying amounts of DPPH. to a polymerising system, and it is noted that fairly sharp inhibition periods are obtained indicating that very little polymerisation occurs during this period. It is seen that in the reaction mixture containing 6×10^{-5} mole.l.$^{-1}$ of DPPH. there is evidence that some polymerisation does occur before the end of the induction period given by extrapolating the steady rate back to the time axis.

Fig.(7) shows that there is a linear relationship between the amount of DPPH. added and the inhibition period produced so that DPPH. is behaving as an inhibitor rather than a retarder.

Fig.(7a) gives the relationship between the rate of removal of DPPH. and the initiator concentration over the range 1.22 - 4.88 x 10^{-3} mole.l.$^{-1}$ of AIBN. The first three points lie on a straight line and the fourth point, corresponding to the highest initiator concentration, is slightly below the line, possibly due to the greater light absorption which occurs due to this AIBN. concentration. (Approx 12%)

It can therefore be concluded that over the above range of initiator concentrations DPPH. may be successfully used to count the available radicals derived from AIBN. by observing the inhibition periods produced in the presence of a polymerisable material such as methyl methacrylate.

Fig.(8) shows the change in optical density which occurs during irradiation, and from a knowledge of the initial DPPH. concentration it is possible to calculate the rate of removal of DPPH. for the initiator concentration used.

Fig.(10) gives the $-d[DPPH]/dt$ against $[AIBN]$ relationship for the various initiator concentrations

used. This again is linear, thus showing that DPPH. can be used to count radicals derived from AIBN. in the presence of methyl methacrylate by the spectrophotometric method.

It will be seen that the rate of removal of DPPH. as obtained by these two methods differs somewhat, the absorption method yielding an apparently higher value. Thus the end point and the inhibition period do not correspond exactly, the end point being too short by comparison with the inhibition period.

Figs. (11) & (12) represent the reaction between DPPH. and AIBN. in the presence of chloroform. The rates of removal of DPPH. are higher in chloroform than in methyl methacrylate. If a fraction of the DPPH. radicals abstract a hydrogen atom from chloroform, this would account for the increased rate of removal. It has been shown in blank experiments however that the rate of removal of colour in a mixture containing only DPPH. and chloroform was very small, so that such a reaction is unlikely to be significant. Some other side reaction must therefore be occurring, causing the destruction of some of the DPPH. radicals.

It should be realised that it is not a reliable procedure to measure the rate of removal of DPPH. in a non - polymerising solvent, and then use this result to deduce the rate of initiation which would

occur in the presence of a monomer. The nature of the solvent used influences the rate of removal of DPPH., and there is a difference of a factor of about 3 in the rate of removal of DPPH. in benzene and chloroform.[48]

It will be seen that the end points of the reactions in Figs. (9) and (11) are considerably different. This gives further indication that the solvent is in some way involved in the reaction. Thomson[49] and Mc.Intosh[48] have also noted differences in the optical densities of the end products formed in the presence of other solvents.

Once the rate of initiation has been evaluated by the methods used it is possible to compare the results obtained and to derive other factors which lead to a clearer understanding of the initiation process. Table (7) summarises the results obtained by all of the methods.

Table (7).

Summary of rates of initiation by various methods.

AIBN.	DPPH. Inh.	DPPH. Spec.	M.Wt.	Tracer	DPPH. in $CHCl_3$
1.22	1.67	1.79	1.04	1.26	1.9
2.44	3.31	3.53	-	2.43	3.8
3.66	5.0	5.3	-	-	5.55
4.88	6.5	7.1	3.65	4.14	-
7.32	-	-	4.59	6.28	-
9.76	-	-	6.98	8.39	-
12.2	-	-	9.48	10.82	-
	Units:- mole.l.$^{-1}$sec.$^{-1}$ x 10^8				

Excluding the results for the rate of removal of DPPH. in chloroform, the molecular weight method gives the lowest value for the rate of initiation, while the spectrophotometric method gives the highest value. The results derived from molecular weights assume that termination is by disproportionation exclusively, but since some combination does occur as shown in table (6) the molecular weight results will be increased by the factor m, the number of initiator fragments per polymer molecule, and the results will then be in close agreement with the tracer results.

The efficiency of initiation.

The difference in the apparent rate of initiation using DPPH. and the radiotracer method may be related to the efficiency of initiation.

If it is assumed that DPPH. reacts with all the available radicals produced in the presence of the monomer, and that each DPPH. radical reacts with only one initiator radical, no regeneration of DPPH. taking place, then the rate of removal of DPPH. is equivalent to the maximum possible rate of initiation of polymer chains. The ratio given by:-
(rate of removal of DPPH.)/(rate of initiation by tracer method) is therefore equal to the maximum efficiency of initiation.

The true efficiency of initiation will be less than this value since those radicals taking part in geminate recombination will be undetected by DPPH. and it is possible that some of the AIBN. may decompose by a non - radical mechanism to give inert products.

In table (8) the data for DPPH. and the tracer method are compared. The maximum efficiency appears to be between 59% and 72%. The value of 72% is probably too high, and examination of Fig.(17) which shows the plot of log.I against log. AIBN. indicates

that the measured values of the rate of initiation are too high for reactions using initiator concentrations of 1.22 and 2.44 x 10^{-3} mole.l.$^{-1}$

On the other hand there is likely to be more error in the determination of the rate of removal of DPPH. at the higher initiator concentrations, since the inhibition periods are shorter. If the rates of initiation corresponding to the lower values of initiator concentration are corrected by assuming that these points should fall on the linear portion of the log.I - log.[AIBN] graph, then the observed efficiencies are in closer agreement. This is shown in table (9).

Table (8)

Efficiency of initiation.

[AIBN.] mole.l $^{-1}$x10^{3}	-d [DPPH]/dt (Average)	I Tracer.	Efficiency. %
1.22	1.73	1.26	72
2.44	3.42	2.43	71
3.66	5.25	3.1	59
4.88	6.8	4.14	61
	Units: mole.l.$^{-1}$sec^{-1}x10^{8}		

Table (9).

Corrected Efficiency of initiation.

[AIBN] mole.l.$^{-1}$ x10^{3}	-d [DDDH] /dt (Average)	I (Corrected.)	Efficiency. %
1.22	1.73	1.11	64
2.44	3.42	2.16	63
3.66	5.25	3.1	59
4.88	6.8	4.14	61

Method of termination.

By comparing the results of the molecular weight method and the tracer method it is possible to determine the process by which termination of growing polymer radicals occurs. The tracer method leads to the kinetic chain length, $\underline{v}$, while the molecular weight method gives the number average degree of polymerisation, so that it is possible to evaluate $\underline{m}$, the number of initiator fragments associated with each polymer molecule formed.

Table (6) gives the values calculated for $\underline{m}$. It is seen than $\underline{m}$ lies between 1.13 and 1.21 with the average value equal to 1.15. As previously stated this

indicates that termination occurs mainly by disproportionation, although a certain amount of combination does occur.in the photochemical polymerisation of methyl methacrylate at 25°C. The value of m obtained agrees well with the results quoted by Bevington, Melville and Taylor[37] for the bulk polymerisation of methyl methacrylate.

Final conclusions regarding the methods used.

Of the various methods used to evaluate the rate of initiation the use of DPPH. as a polymerisation inhibitor leads to a quick estimation of the rate of initiation particularly if the spectrophotometric method is used. There is the uncertainty associated with the efficiency of initiation, but once this has been established absolute values for the rate of initiation can be deduced from $- d[DPPH]/dt$.

If therefore it is desired to evaluate rates of initiation in a system for which the efficiency of initiation is known, the use of DPPH. is convenient and will lead to reasonable values in most cases. In some monomers the use of DPPH. leads to erroneous values for the rate of initiation, e.g., 2 - vinyl pyridine, as indicated in part two of this thesis. Also, it has been shown by Bengough[50] that DPPH. should not be employed to measure rates of

initiation when the monomer can react with nitro groups.

The main disadvantage with the molecular weight method is the uncertainty about the termination step, unless of course this has previously been established for the monomer being considered. In cases where DPPH. cannot be used and the mode of termination is known, the molecular weight method would be very useful.

The radiotracer method leads to an unambiguous value for the rate of initiation, provided the experimental inaccuracies are kept to the absolute minimum, the results by this method are the most reliable available. The radiotracer method is of particular value where no chain transfer occurs, and in such a case the errors incurred in the evaluation of the rate of initiation can be reduced to a very small value. The error in the determination of the rate of polymerisation and in the recovery of the polymer is normally small and the error in gas counting can be made very small by counting for a sufficiently long period in a sealed tube. The method can be successfully applied in conditions where chain transfer occurs, but in this case the amount of transfer occurring must be known, so that a correction can be made.

It is a combination of all of the methods which have been used in this work which gives the maximum information about the initiation process. Thus, the efficiency of initiation and the process by which termination occurs can also be established.

The equipment required for the tracer method is more complex and more expensive than the simpler equipment used in the other methods, but this disadvantage can be set against the greater reliability and the greater scope of the radiotracer technique.

The radiotracer technique can also be applied to other processes associated with polymerisation and direct information obtained about the nature of these processes. The effect of a solvent or chain transfer agent can be studied by using a labelled solvent or transfer agent. The effect of using a combination of two initiators can be studied by labelling one of the initiator and the technique can also be applied to a study of co - polymerisation processes.

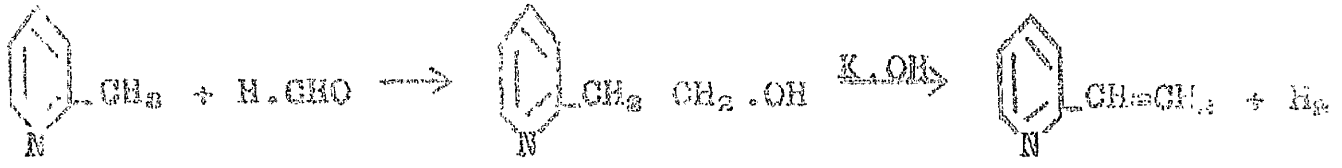
P A R T T W O.

THE PHOTOCHEMICAL POLYMERISATION OF 2 - VINYL PYRIDINE.

C H A P T E R 5.

INTRODUCTION.

There are three vinyl - pyridine isomers:- 2- or α- , 3- or β- , 4- or γ- . The monomer 2 - vinyl pyridine has been known since 1889 when it was prepared by Landenburg[51] from α - picoline isolated from coal tar:-



The pure monomer is a colourless mobile liquid of pungent, unpleasant odour. It is a lachrymatory substance and a skin irritant and must be handled with the same care as pyridine. The monomer is soluble in the common organic solvents and about 2.5% dissolves in water at room temperature. It is soluble in dilute

aqueous acids, with which it forms vinyl - pyridinium salts. The polymer is somewhat similar in appearance to polystyrene, but it swells in water and dissolves in dilute acids.

Poly 2 - vinyl pyridine and some copolymers have several industrial uses. These include use in adhesives, in the anti - halation layer in photographic emulsions, while copolymers containing 2 - vinyl pyridine are used in the preparation of basic ion exchange resins and a copolymer with acrylonitrile is of considerable interest as a fibre since it can be dyed easily with acid type dyes. Poly N - vinyl pyridinium halides and other quaternary salts are of interest as surfactants and fungicides.

Little interest or attention has been given to the polymerisation of the monomer in bulk, but there has been a considerable amount of work done on the copolymerisation of 2 - vinyl pyridine with various monomers. Systems studied include 2 - vinyl pyridine with acrylonitrile, butadiene, butyl acrylate, methyl methacryiate, and styrene.

Natta et al. [52] have described the preparation of crystalline stereospecific polymers of 2 - vinyl pyridine using Et_3NMgBr and PhMgBr as catalyst. Analysis showed that the end groups of the polymer contain the ethyl or phenyl groups derived from the

catalyst and both the N atom and the double bond are co - ordinated to the growing radical as monomer is added, thus causing a constant type of presentation of monomer and resulting in a regular polymer. It is suggested that the reason why 4 - vinyl pyridine does not give similar crystalline stereospecific polymers is because the N atom is too far removed from the double bond to permit the above type of bond.

Duling & Price[53] have described the preparation and reactions of some N - vinyl pyridinium salts. These were found to polymerise and copolymerise with both ionising radiation and free radical initiation.

In a paper by Onyon[54] the polymerisation of 4 - vinyl pyridine was discussed. A number of interesting features were noted, including the detection of a surface catalysed heterogenious reaction.

In this work a simple kinetic study of the polymerisation of 2 - vinyl pyridine has been undertaken. Most of the measurements have been confined to the initial stages of polymerisation, say not more than 6% reaction, because of complications which arise due to a slight colour change which has been observed in the polymerisation of the monomer at higher conversions.

The rate of initiation has been measured by the radiotracer method. DPPH. proved unsuitable as

an inhibitor since the measured rate of consumption of DPPH. appeared to be too great. The constants for the propagation and termination reactions, K_p and K_t, have been evaluated using the thermocouple non - stationary state method and the rotating sector method. The activation energies and heat of polymerisation have also been measured.

Some evidence for a heterogenious reaction has been noted during the polymerisation of the monomer to 10 - 15% . when the monomer was being prepolymerised to this extent on the vacuum line small white specks of polymer were seen in the reaction mixture.

There is also some evidence to indicate the occurence of the "gel effect", and unlike a number of other monomers, a thermal dark rate has been found.

A brief examination of the monomer 4 - vinyl pyridine was carried out and the results compared with the data for 2 - vinyl pyridine.

Determination of the individual rate constants.

The three quantities which can be readily found experimentally in a polymerisation reaction are:-

1) the reaction rate, $-d M / dt$;

2) the number average degree of polymerisation; and

3) the kinetic chain length.

From these quantities it is not possible to evaluate K_p and K_t separately since they only occur as ratios in the overall rate equation, (1.10)

To evaluate the constants it is therefore necessary to determine other relationships between the constants, or to establish quantities which involve only one of the constants. These additional relationships can be found by measurement of reaction rates using a non - stationary state method. An alternative method is based on "pseudo - stationary" states. Physical conditions are selected so as to attain a stationary state which is determined by physical rate processes as well as by chemical reaction rates.

In this work measurements have been made by a non - stationary state technique and by a "pseudo - stationary" state method. In order to apply these methods it is essential that the following conditions are satisfied:-

1) the time of the start of the reaction must be accurately known. This is readily found for a photochemical reaction;

2) an accurate method of measuring the rate of reaction must be available and of sufficient sensitivity to detect the small variations involved;

3) all reactants must be of extremely high purity to prevent initial inhibition periods or chain transfer reactions involving the impurities.

The second condition is the most difficult to satisfy, but there are now a number of methods available for evaluating the rate of reaction. For the non - stationary state reaction methods which have been used to obtain the velocity coefficients include direct measurement of the temperature rise in the reaction vessel using a thermistor[55], or a thermocouple[56] and a method which measures the temperature rise as a function of the dielectric constant[57,58]. All of these methods are based on the assumption that the conditions remain adiabatic within the reaction vessel during the period of reaction. Bengough[59] has given a dilatometric method of measuring the initial expansion of the reactants, and provided adiabatic conditions are maintained in the reaction vessel, this can be correlated to the absolute rate of reaction. Benson & North[60] have used a simple dilatometric method which uses the decay curve obtained immediately following the end of irradiation. The cooling effects are allowed for and it provides a useful method for the initial stages of reaction, particularly if the radical lifetime is long. This is a non - adiabatic, non - isothermal

method.

"Pseudo - stationary" state methods which have been used include the rotating sector[61,62] and spacial interference techniques[63,64].

The non - stationary state thermocouple method[56].

A thermocouple of negligible heat capacity is situated at the centre of the reaction vessel in which the rate can be measured dilatometrically if required. When polymerisation takes place the temperature rise causes an emf. to be set up at the thermo - junction. The relationship between emf. and temperature is known and provided the emf. can be amplified sufficiently to be conveniently measured, the rate of reaction can be easily obtained.

The reaction vessels are easily made and are expendible so that the method can be used over the entire range of polymerisation.

The rotating sector method.[57,58].

A reaction vessel in a thermostatically controlled tank is subjected to intermittent ultraviolet irradiation. The periods of light and dark are governed by the size of the segment cut out of the rotating disc and the speed of rotation of the disc. By measuring the rate of reaction at full illumination by dilatometry and at a range of different sector

speeds it is possible to calculate the kinetic chain lifetime. The disadvantage of this method is that polymerisation proceeds to a considerable extent during rate measurement. This disadvantage is eliminated in the modified rotating sector technique described by Bengough et al. [65] who measured the rate as a function of the initial expansion which occurs when the mixture is irradiated under adiabatic conditions.

The method described in this work, the use of the non - stationary state thermocouple technique also eliminates the disadvantages of the original sector method.

Theory of the non - stationary state reaction.

Applying the theory given by Burnett[66] to the reaction scheme set out in pages 4 - 6 of this thesis, and assuming that the termination step occurs by mutual reaction of two polymer radicals, i.e.(1.4), then,

$$d[R]/dt = I - K_t[R_s]^2 = 0. \qquad \ldots(5.1)$$

when the stationary state has been reached.

Thus,

$$[R_s] = (I/K_t)^{0.5} \qquad \ldots(5.2)$$

During the non - stationary state, the

concentration of radicals is altering continuously, and, integrating (5.1),

$$0.5(K_t I)^{0.5} \times \ln. \left[\frac{1 + (K_t/I)^{0.5} M}{1 - (K_t/I)^{0.5} M} \right] = t + C \qquad \ldots(5.3)$$

and C = 0, since R = 0 at t = 0.

$$\therefore \quad \tanh^{-1} \frac{[R]}{[R_s]} = (K_t I)^{0.5} = \frac{t}{\tau} \qquad \ldots(5.4)$$

where τ represents the lifetime of the growing chain.

From (5.4) $$[R] = [R_s] \tanh \frac{t}{\tau} \qquad \ldots(5.5)$$

Now, the rate of removal of monomer at any instant is given by:-

$$-d[M]/dt = K_p [R][M] \qquad \ldots(5.6)$$

i.e., $$-d[M]/dt = K_p [R_s][M] \tanh \frac{t}{\tau} \qquad \ldots(5.7)$$

Integrating (5.7) gives:-

$$- \ln \frac{[M]}{[M_o]} = \frac{K_p}{K_t} .\ln.(\cosh \frac{t}{\tau}) \qquad \ldots(5.8)$$

where $[M_o]$ is the initial monomer concentration and $[M]$ is the monomer concentration at any instant.

If F is the fraction of monomer converted to

polymer, then,

$$[M]/[M_o] = (1 - F) \qquad \ldots(5.9)$$

$$\text{i.e.,} \quad -\ln.(1 - F) = \frac{K_p}{K_t} \ln. \cosh\left(\frac{t}{\tau}\right) \qquad \ldots(5.10)$$

$$\text{Now, if } F \quad 1, \quad -\ln.(1 - F) = F \qquad \ldots(5.11)$$

$$\therefore \quad F = \frac{K_p}{K_t} \ln. \cosh \frac{t}{\tau} \qquad \ldots(5.12)$$

and when t , i.e., during the stationary state,

$$F = \frac{K_p}{K_t} (t/\tau - \ln.2) \qquad (5.13)$$

A plot of fractional conversion, $\underline{F}$ against $\underline{t}$ gives a straight line of slope $K_p/K_t \cdot \tau$ and an intercept on the time axis of $\tau \ln.2$.

The lifetime may also be obtained from the decay curve produced when irradiation is stopped. When this happens the production of radicals by initiation ceases and the concentration of radicals is reduced by termination.

$$\text{i.e.,} \quad d[R]/dt = -K_t[R]^2 \qquad \ldots(5.14)$$

Integrating,

$$[R] = \frac{[R_s]}{(t/\tau + 1)} \qquad \ldots(5.15)$$

$$\therefore \quad F = \frac{K_p}{K_t} \ln.(t/\tau + 1) \qquad \ldots(5.16)$$

A plot of F against t will have an intercept on the time axis of $\gamma \ln.2$.

By stationary state measurements it is possible to determine ratios of the velocity coefficients in two ways:-

1) from the overall rate equation, (1.10) the ratio $K_p/K_t^{0.5}$ can be obtained; and

2) the intercept on the time axis of the straight line portion of the fractional conversion curve is $\gamma \ln.2$ and therefore, if the recording system has an instrument lag of C seconds, the equation relating the rate of reaction and the measured intercept, X, can be written:-

$$\frac{1}{\text{Rate}} = \frac{K_t}{K_p} \cdot \frac{X}{\ln.2} + C \qquad \ldots(5.17)$$

and thus by plotting the reciprocal reaction rate and the measured intercept, a straight line of slope $K_t/K_p \cdot \ln.2$ and intercept on the time axis equal to C is obtained.

Hence the ratio K_t/K_p can be evaluated. Also, from (5.4), $\gamma = 1/(K_t I)^{0.5}$ so that K_t can be found. Thus both K_p and K_t can now be evaluated.

This analysis of the kinetics of vinyl polymerisation is based on reactions which are known to occur in the bulk polymerisation, i.e., when pure monomer is being polymerised. It is also an ad hoc postulate that termination occurs by mutual interaction of polymer radicals, i.e., the termination process is second order with respect to R. In the presence of some materials, e.g., a retarder, the termination will be a first order process.

In those cases where termination occurs by both first and second order reactions, serious errors will be incurred in the above scheme, but a method has been given by Burnett & Wright[66] for correcting for mixed order termination in reactions of this type. The application of their treatment is difficult in many cases and cannot be conveniently used in the later stages of polymerisation or for heterogenious reactions. In some cases, where experimental results have indicated that the termination process is of a mixed order, the kinetic treatment has been based on the assumption that second order kinetics apply. Bengough & McIntosh[48] have given a method which eliminates the errors due to the assumption of second order kinetics by introducing a correction factor.

The theory of the modified rotating sector method.

The use of intermittent light to determine velocity coefficients was first suggested by Briers et al. [67] in 1926 but the first significant application to the field of liquid phase polymerisation was in 1945 when several workers determined the velocity coefficients in the polymerisation of vinyl acetate [61,62].

Bengough et al. [65] have described the theory of the modified rotating sector method, and since the technique is now well known, it need not be given in detail in this thesis.

In this work, for a sector giving equal light and dark periods, it can be shown that when the flash time is equivalent to the radical lifetime, γ, then the ratio;-

$$\frac{\text{Reaction rate with intermittant irradiation}}{\text{Reaction rate with steady irradiation}} = 0.694$$

By measuring the reaction rate at a series of different sector speeds and plotting a graph of sectored rate/steady rate) it is therefore possible to evaluate γ, and hence K_t by using the relationship $\gamma = 1/(K_t I)^{0.5}$

K_p can then be found by substituting the value

of K_t found in the ratio $K_p/K_t^{0.5}$.

C H A P T E R 6.

EXPERIMENTAL.

Materials.

2 - vinyl pyridine. This was obtained from Polymer Consultants Ltd., and contained 0.1% ter - butyl catechol as inhibitor. A few pellets of solid potassium hydroxide were added to a sample of the monomer and this was distilled through a 24" packed column operating at high reflux ratio, the first and last fractions being rejected. The fraction boiling at 72°C (30 mm.) was collected. This fraction was redistilled through the column, the first and last fractions again being rejected.

This sample was transferred to a distillation flask containing a little AIBN. and attached to the vacuum line. It was thoroughly prepolymerised to at least 10% conversion, after which it was distilled under vacuum and again prepolymerised to about 10%

conversion . The monomer was distilled off and kept at -78°C until required for use. It was found necessary to use high vacuum silicone grease on the taps and the monomer had to be heated to about 40°C to enable vacuum distillations to be carried out in a reasonable time.

Apparatus.

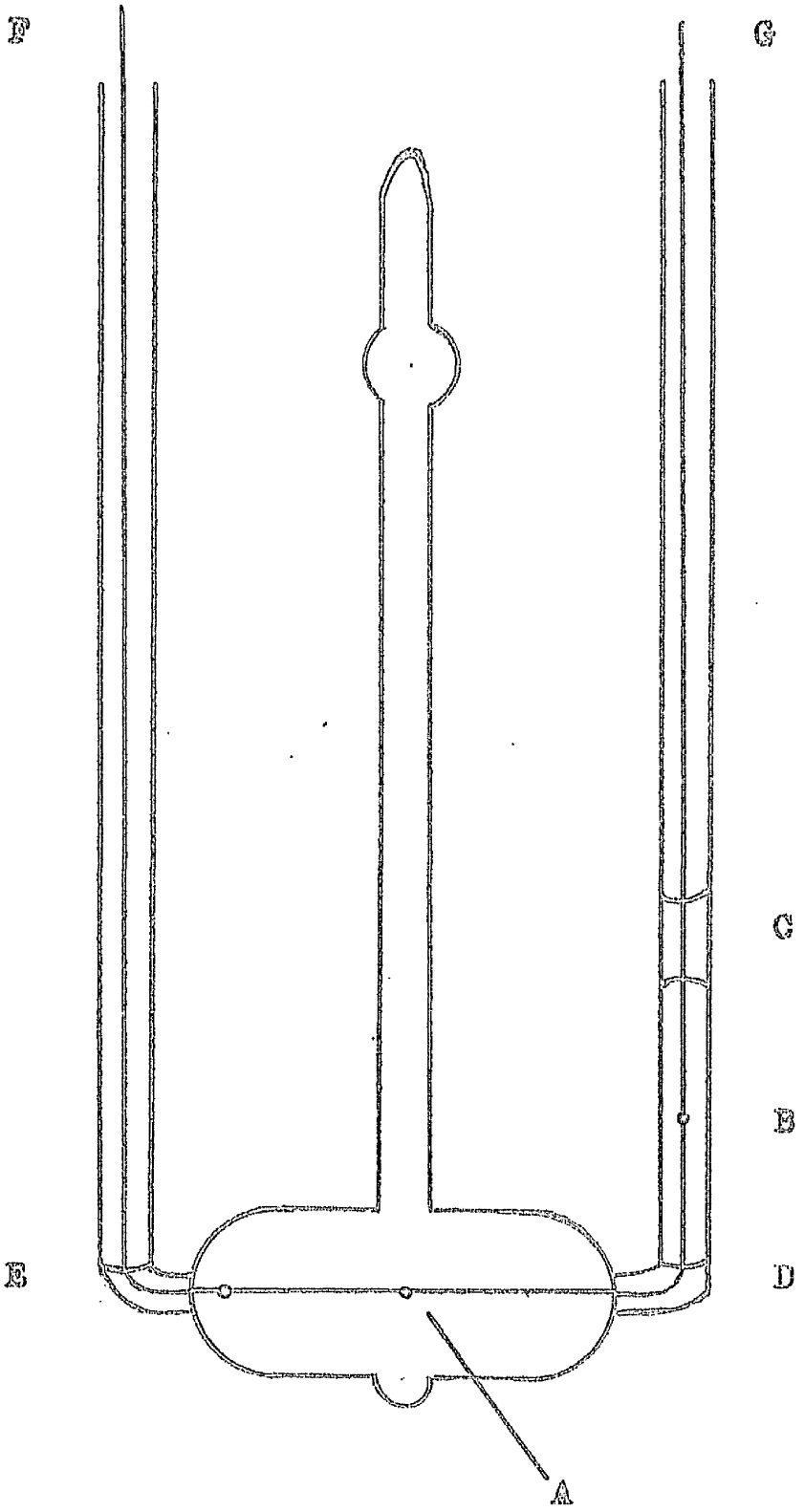
Equipment required for the thermocouple method.

The apparatus required consisted of the reaction vessel described below, a constant temperature water bath, an amplifier and a recording voltmeter. A mercury vapour lamp was used to provide ultraviolet radiation and a Chance OX1 filter was used.

The reaction vessel is shown in Fig.(18). It consists of a dilatometer in soft soda glass with two additional side arms. The thermocouple system consisted of two thermojunctions, one situated at the centre of the reaction vessel and another in one of the side arms to act as the cold junction. Wires EA and AB were of 34 swg. copper and constantin wire respectively, while the connecting leads FE and GB were borated iron - copper clad wire, which is suitable for sealing into soft soda glass.

The thermocouple system was made by brazing lengths of the 34 swg. wires to the connecting leads

The thermocouple vessel. Fig.(18)



with a small piece of silver solder. The length of each wire required for each particular reaction vessel was then measured off and the 34 swg. copper and constantin wires twisted together. The junction was silver soldered and trimmed with a pair of small pliers to give a very small junction. The junctions were thoroughly cleaned with very fine emery cloth and rinsed in hot water.

The complete thermocouple system FG was threaded through the dilatometer so that one thermojunction was in the centre of the dilatometer bulb, and the other was in the centre of the jacket in the side arm. Constrictions E and C were collapsed to give vacuum tight seals, and the side arm FE was bent up parallel to the stem. The vessel was then attached to the vacuum system and thoroughly evacuated. The constriction at D was then collapsed about the constantin wire, giving a seal which was liquid tight but not air tight. The vessel was kept under vacuum until required for use and was exposed to the air for the minimum of time during calibration.

The amplifier was a Tinsley No.5132 D.C. type amplifier which is designed for an input impedance of less than 10 ohms. It is particularly suited to this system since it is capable od giving a voltage amplification of more than 10^6. Emfs. of up to

400 microvolts in the input circuit could be balanced out by course or fine controls.

The temperature rise is calibrated by means of a test signal varying from 0.1 to 10 microvolts as required. and the output circuit gave a current of up to 10 milliamps.

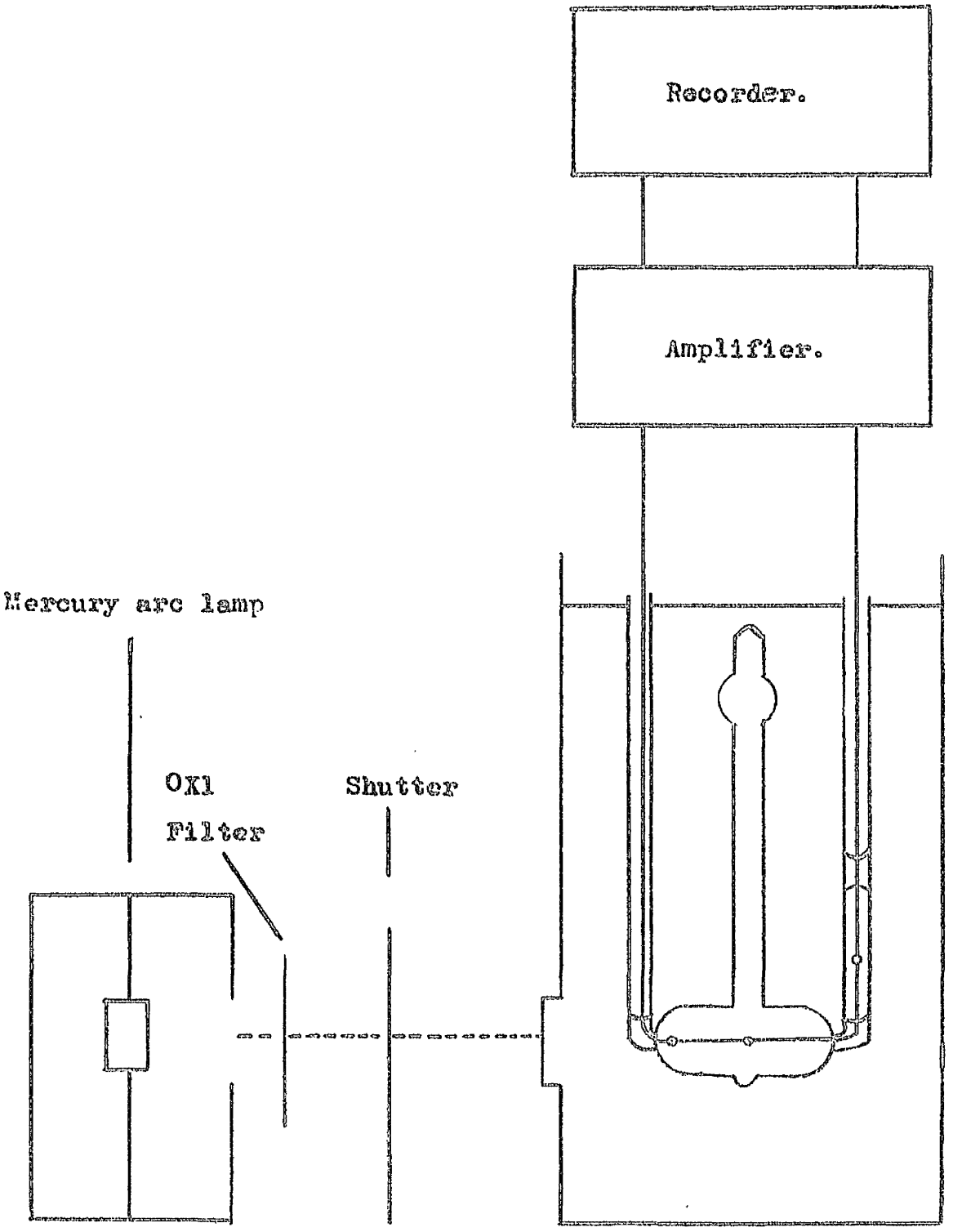
A shutter was placed between the UV lamp and the reaction vessel. This shutter was removed by hand at the start of each reaction.

An Elliot pen recording voltmeter gave a chart trace of the output signal from the amplifier. During the reaction the chart was operated at a speed of 12" per minute, but this speed could be quickly reduced to 12" per hour by a clutch mechanism when the reaction was over. Fig.(18a) shows circuit layout.

Apparatus used in the rotating sector method.

The reaction was carried out in a vessel of the type just described, the rate of reaction being found by the thermocouple method. The reaction rate was varied by causing a circular disc to rotate at varying speeds in front of the UV lamp. The disc was 18" in diameter and had segments cut out to give equal light and dark periods. The disc was driven by an electric motor whose speed could be varied by a potentiometer control. The speed of rotation of

Layout for the thermocouple technique. Fig.(18B)



the disc was measured during the reaction by a magnetic impulse counter which was operated by a cam fitted to the driving shaft.

Procedure.

Non stationary state technique.

The filled reaction vessel was placed in the water bath, care being taken to ensure that no water entered the side limbs. Light PVC. sleeving was slipped over the conecting leads and inside the side arms. The sleeving was sealed in with Bostik No.1 adhesive. The connecting leads were soldered to leads from the input circuit of the amplifier. When the adhesive was dry more water was added to the water bath, the amplifier and the mercury vapour lamp were switched on and about 30 minutes was allowed for them to reach stable operating conditions before any measurements were made.

The monomer was polymerised to not more than 2% conversion before taking any measurements.

With a chart speed of 12" per minute and a known voltage was put through the circuit for about 5 seconds to calibrate the system at the desired amplification, and the chart was allowed to run at this speed for a further period to ensure a steady temperature before starting irradiation. The stirrer

was switched off during this period in reactions at 15°C and 25°C.

At a predetermined time the shutter was removed manually. The rise in temperature of the reaction was observed on the trace and when a steady rate of temperature increase was reached the shutter was replaced, thus stopping the reaction.

From the chart trace the rate of reaction in microvolts per second and the intercept in seconds on the time axis were found. The rate of reaction was varied by inserting wire gauze screens of known light transmission in front of the light beam and then repeating the above procedure. A graph of reciprocal rate against measured intercept was drawn and the instrument lag, $\underline{C}$, found. From the slope of the graph K_t/K_p was calculated.

Individual rate measurements were repeated several times, all the results quoted being average values.

Precipitation of Polymer.

Polymer was isolated from the partly polymerised mixture by precipitation. A benzene solution of the polymer - monomer mixture was added to a ten fold excess of n - hexane, dropwise and with constant stirring. The fine precipitate obtained was allowed

settle and then filtered through a No.3 porosity scintered glass crucible and the polymer thoroughly rinsed with n - hexane to remove traces of monomer and initiator.

Samples required for molecular weight measurement, or for the determination of the rate of initiation by the radiotracer method were dissolved in benzene and two further reprecipitations carried out. The final precipitated polymer was dissolved in benzene and freeze - dried.

Determination of the yield of polymer.

The relationship between the rate of contraction and the rate of polymerisation must be known so that simple dilatometric rate measurements can be expressed as absolute rate units. The relationship was established by measuring the rate of contraction in a simple dilatometer and immediately precipitating the polymer obtained. In this case only one precipitation was carried out to minimise handling losses. The polymer was slowly dried to constant weight and the amount of polymerisation which had occurred was calculated. This was equated to the % contraction, and the result expressed in the form 1% contraction = X% polymerisation.

Molecular weight measurements.

The molecular weight of a series of polymers

was found using the Pinner - Stabin osmometer, as previously described. The solvent used was benzene.

Determination of the specific heat.

The specific heat of the monomer was found by making application of Newton's Law of Cooling. This law states that for any given volume, having a stated surface area, the rate of cooling at any given temperature is proportional to the heat capacity of the material.

If the rate of cooling of a liquid of unknown specific heat is compared to the rate of cooling of another liquid of known specific heat, cooling under the same conditions, then the specific heat of the first liquid may be found from:-

$$dT_a/dt.(W_a.S_a + E) = dT_b/dt.(W_b\ S_b + E) \quad ..(6.1)$$

where W and S represent the weight and specific heat heat of the liquids, dT/dt is the rate of cooling, and E is the water equivalent of the containing vessel. Subscripts a and b denote the two liquids.

The water equivalent, E, may be measured, or alternatively by comparing the rate of cooling of the monomer with two other liquids of known specific heat, E may be eliminated and the specific heat found.

A glass tube of 1" diameter and 4" length was

fitted with a stopper through which passed a thermometer and a light stirrer. The tube was fitted inside an air jacket of 3 - 4" diameter, such that it was not in direct contact with the air jacket. The rate of cooling between 30°C and 25°C was measured in a constant temperature bath at 25°C.

C H A P T E R 7.

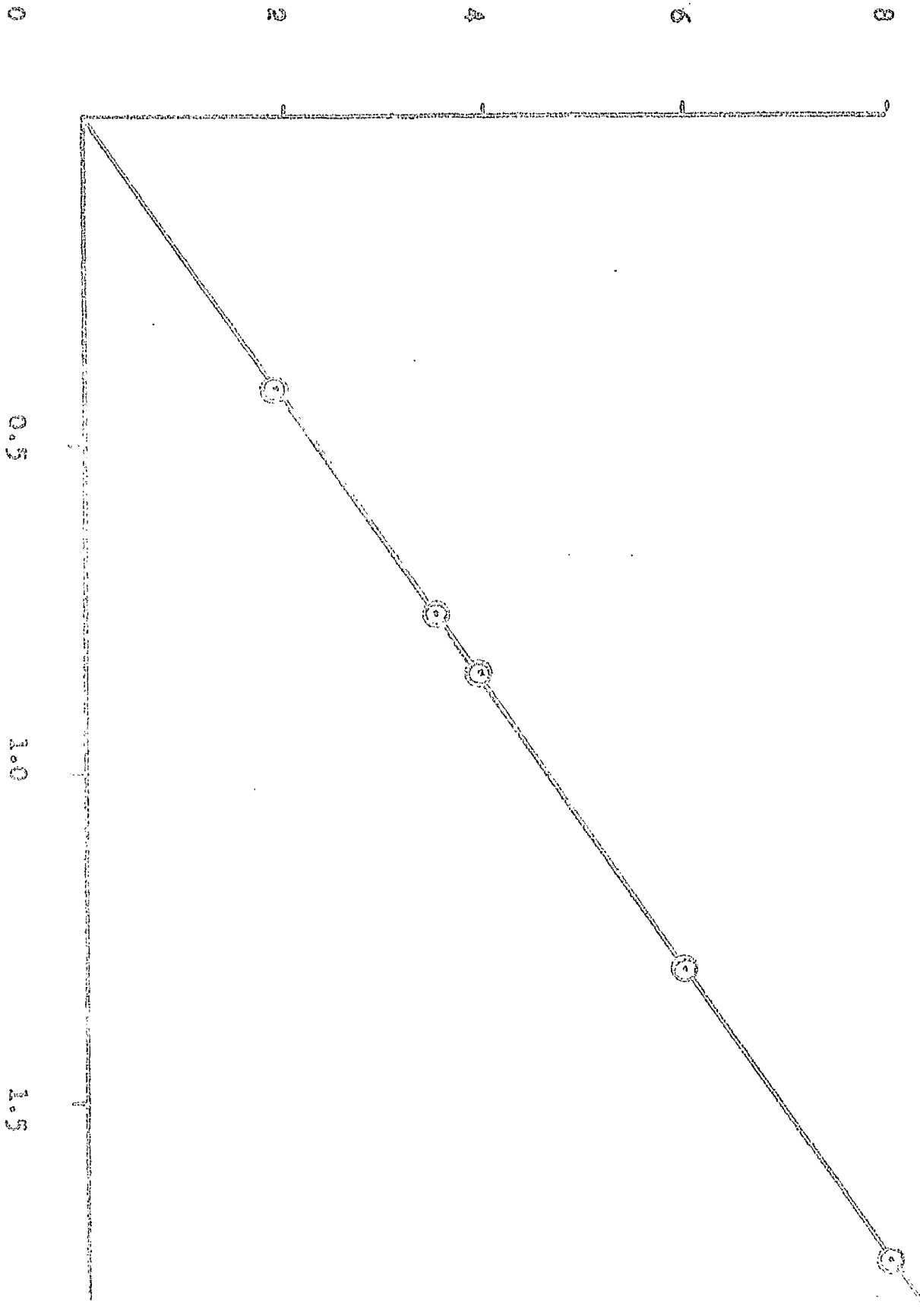
RESULTS.

Relationship between % contraction & % polymerisation.

Several polymerisations were carried out and the polymer isolated from the reaction mixtures at different extents of reaction. The amount of polymer which had formed was determined and a graph of % contraction against % polymerisation was drawn as shown in Fig.(19) From the slope of this graph the relationship between % contraction and 4 polymerisation is:-

1% contraction = 4.6% polymerisation, at 25°C.

This relationship applies over the range in which all dilatometric rate measurements were made.



Dependence of the rate of polymerisation on the initiator concentration.

The rate of polymerisation was measured at several different initiator concentrations, using both active and inactive AIBN. A plot of rate of polymerisation against $\sqrt{\text{initiator concentration}}$ is shown in Fig.(20)

This plot is linear, and allowing for experimental error, is seen to pass through the origin. A log.rate against log. AIBN. plot of these results is given in Fig.(21). This has a slope of 0.51.

It is thus clear that over the first stages of reaction 2 - vinyl pyridine shows second order termination.

Dependence of the rate of reaction on the intensity of illumination.

The dependence of the rate of polymerisation on the intensity of irradiation is usually expressed in terms of an intensity exponent.

The intensity exponent, n, is defined as the slope of the curve relating log. rate and log.intensity, i.e.,

$$n = \frac{d(\log.\text{rate})}{d(\log.\text{intensity})} \qquad \ldots(7.1)$$

Graph of Rate against $\sqrt{AIBN.}$

Exp. (20)

Graph of $\log_{10}(\text{Ratio})$ against $\log_{10}[\text{Ion}]$

Exp. (23)

The intensity of illumination is varied by using wire gauze screens of known light transmission and a plot of log.rate against log.relative intensity is shown in Fig.(22). It is seen that n has a value of about 0.5

It can again be concluded that the termination step is second order, or that first order termination is relatively unimportant in the polymerisation of 2 - vinyl pyridine.

Fig.(23) shows a plot of $1/\overline{DP}_n$ against $\sqrt{AIBN}$. and indicates that very little chain transfer occurs.

Dark rate in photochemical polymerisation.

A dark rate, i.e., a rate of reaction occurring when the monomer is not being irradiated has been observed. This rate has been observed both in the presence and absence of initiator, so that thermal decomposition of the initiator is not the only reaction causing polymerisation to occur.

In the presence of initiator:-

A photochemical rate of 2.48×10^{-5} mole.l.$^{-1}$sec.$^{-1}$ was observed.

After 16 hours, during which the reaction vessel was not irradiated, a rate of 1.48×10^{-6} mole.l.$^{-1}$sec.$^{-1}$ was observed.

Intensity Exponents.

Fig. (22)

$10^4/\overline{DP}_w$
0
2
4
6
0.02
0.04
0.06
0.08

$$\text{Ratio} \quad \frac{\text{Dark rate}}{\text{Photo rate}} = \frac{1.48 \times 10^{-6}}{2.84 \times 10^{-5}} = 0.052$$

In the absence of initiator:-

Photochemical rate = 3.26×10^{-6} mole.l.$^{-1}$sec.$^{-1}$

Rate after 16 hours = 1.25×10^{-6} mole.l.$^{-1}$sec.$^{-1}$

$$\text{Ratio} \quad \frac{\text{Dark rate}}{\text{photo rate}} = \frac{1.25}{3.26} = 0.385$$

Thus it is seen that the dark rate is not due only to initiator decomposition, but is also dependent on the monomer.

Gel effect.

Some indication of the presence of a gel effect has been noted. After about 8% polymerisation the formation of a light brown colour tends to reduce the rate of reaction by reducing the light intensity, but at higher conversions this effect is offset by the gel effect which causes an increase in the reaction rate.

Table (10) indicates the variation in the rate of reaction with differing % reaction. The % polymerisation figures are approximate.

Table (10).

Illustration of gel effect.

Conversion. % Poln.	Reaction rate. Relative units.
1 - 5	1
8	0.95
12	1.23
15	1.52
18	1.68
22	1.83

The rates of reaction were measured by the thermocouple method, and the observed radical lifetime also increased at the higher conversions.

Measurement of the rate of initiation.

The rate of initiation was calculated using the radiotracer method. For 2 - vinyl pyridine, the average composition of the polymer prepared using AIBN. may be expressed:-

$$(C_7H_7N)_n(C_4H_6N)_m \text{ , where } \underline{n} = \overline{DP}_n$$

and $\underline{m}$ = no. of initiator fragments per polymer molecule.

If active AIBN. is used, then:-

$$\frac{\text{Specific activity of carbon in polymer}}{\text{Specific activity of carbon in initiator}} = \frac{4m}{7n + 4m}$$

$$= \frac{4m}{7n} \quad ..(7.2)$$

for a high polymer.

$$\therefore \quad I = R_p \cdot \frac{7 \times \text{polymer activity}}{4 \times \text{initiator activity}} \quad ....(7.3)$$

The rate of initiation was measured at several initiator concentrations. The results obtained are expressed in Fig.(24) which shows the plot of log.I against log.[AIBN.] The slope of this graph is 0.98, again showing that within experimental error, the polymerisation of 2 - vinyl pyridine follows the simple kinetic scheme over the first 6% reaction.

Rate of initiation using DPPH.

When it was attempted to measure the rate of initiation using the inhibitor DPPH. very short inhibition periods were obtained, even with low concentrations of initiator. The calculated rates of removal of DPPH. were about 3 times faster than the results obtained by the tracer method.

When polymerisation was carried out with DPPH.

Graph of log.I against log[AIBN] Fig.(24)

but no AIBN. it was noted that the colour faded quickly, but no contraction occurred for a longer period.

When polymerisation was performed in the presence of 1:3:5 trinitrobenzene (1.2×10^{-4} mole.l.$^{-1}$) complete inhibition was observed for much longer periods than with DPPH.

No inhibition was produced by benzoquinone, catechol, or hydroquinone.

It was therefore concluded that the inhibition produced by DPPH. was in part due to reaction of the nitro groups of the DPPH. with 2 - vinyl pyridine. It has previously been shown by Bengough[50] that where the monomer can react with nitro groups, then DPPH. should not be used in the determination of the rate of initiation.

When DPPH. was used as a radical scavenger, the observed rate of removal of DPPH. in chloroform was much less than in the presence of the monomer, and corresponded more closely with the radiotracer results.

Molecular weights and kinetic chain lengths.

The number average molecular weight, and hence $\overline{DP}_n$ of the polymers used in the determination of the

the rate of initiation by the radiotracer work was measured.

The molecular weight and $\overline{DP}_n$ of these polymers are given in table (11). The kinetic chain length was calculated and m, the number of initiator fragments per polymer molecule evaluated.

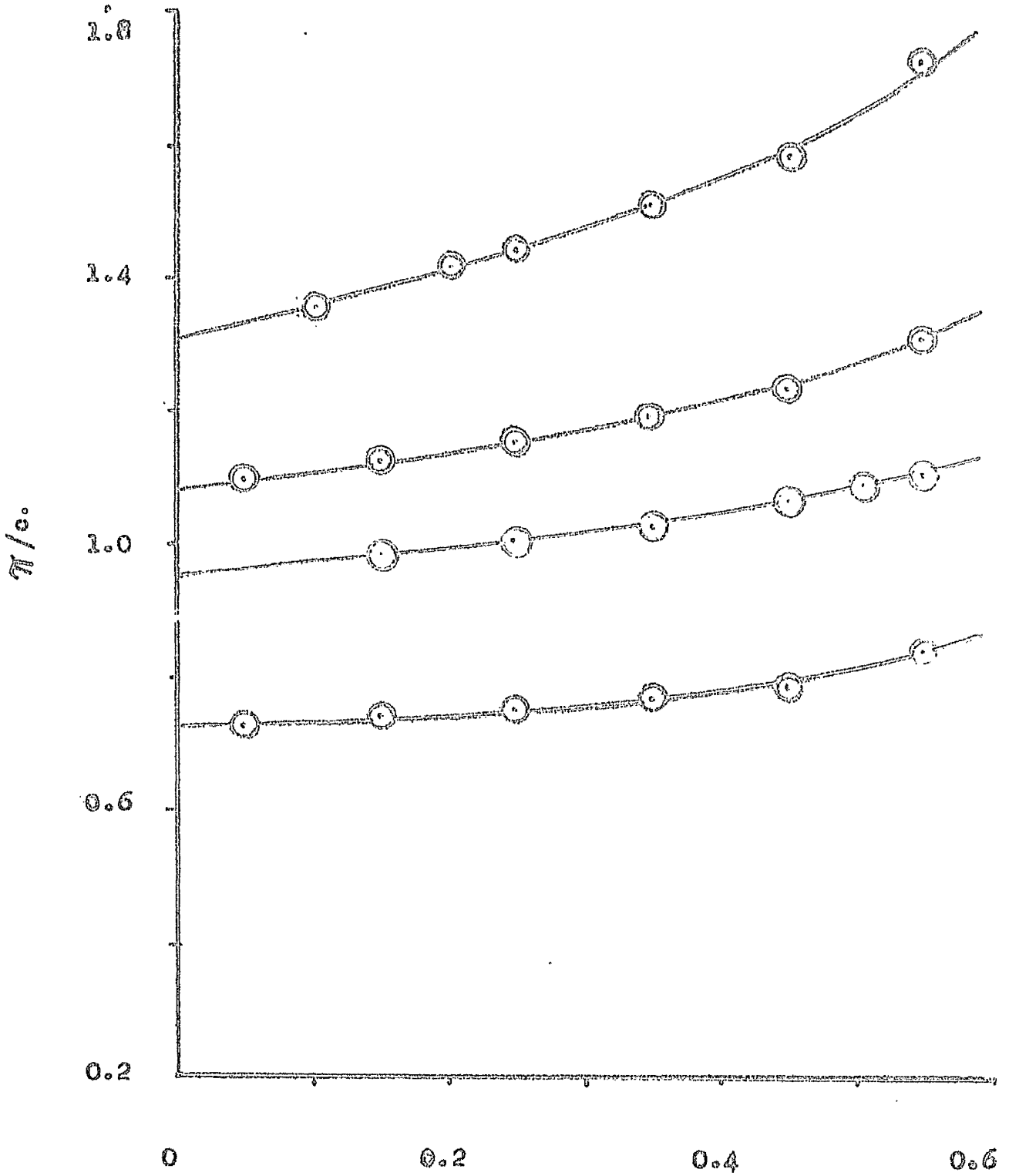
Table (11),

Molecular weights and kinetic chain lengths.

AIBN.	M.Wt.	DP_n	v	m
2.44	394,000	3750	1900	1.98
3.66	306,000	2920	1549	1.89
4.88	270,000	2570	1322	1.95
6.10	221,200	2120	1107	1.92

It is seen that m is approximately equal to 2 so that termination of the growing chains occurs almost exclusively by combination.

Fig.(25) shows the π/c against c curves for these polymers. c is in gm. polymer per 100 cc. benzene soln.


1.8
1.4
1.0
0.6
0.2
π/c
0
0.2
0.4
0.6
c (gm. polymer/100 cc benzene)

Evaluation of K_p and K_t.

Using the thermocouple method, the ratio K_t/K_p has been determined at 15°C, 25°C, and 35°C. Fig.(26) shows a typical trace of the reaction, and Fig.(27) gives the plot of 1/Rate against the measured intercept, X, at 25°C

For the polymerisation at 25° C, the following data has been found;

Rate of polymerisation = 0.0933 μv.sec^{-1} by thermocouple method.

= 2.88 %poln.hour^{-1}, by dilatometry.

= 7.45×10^{-5} mole.l.$^{-1}$sec.$^{-1}$

= 8.0×10^{-6} sec.$^{-1}$

Thus, a rate of 1 μv.sec.$^{-1}$ = 8.6×10^{-5} sec.$^{-1}$

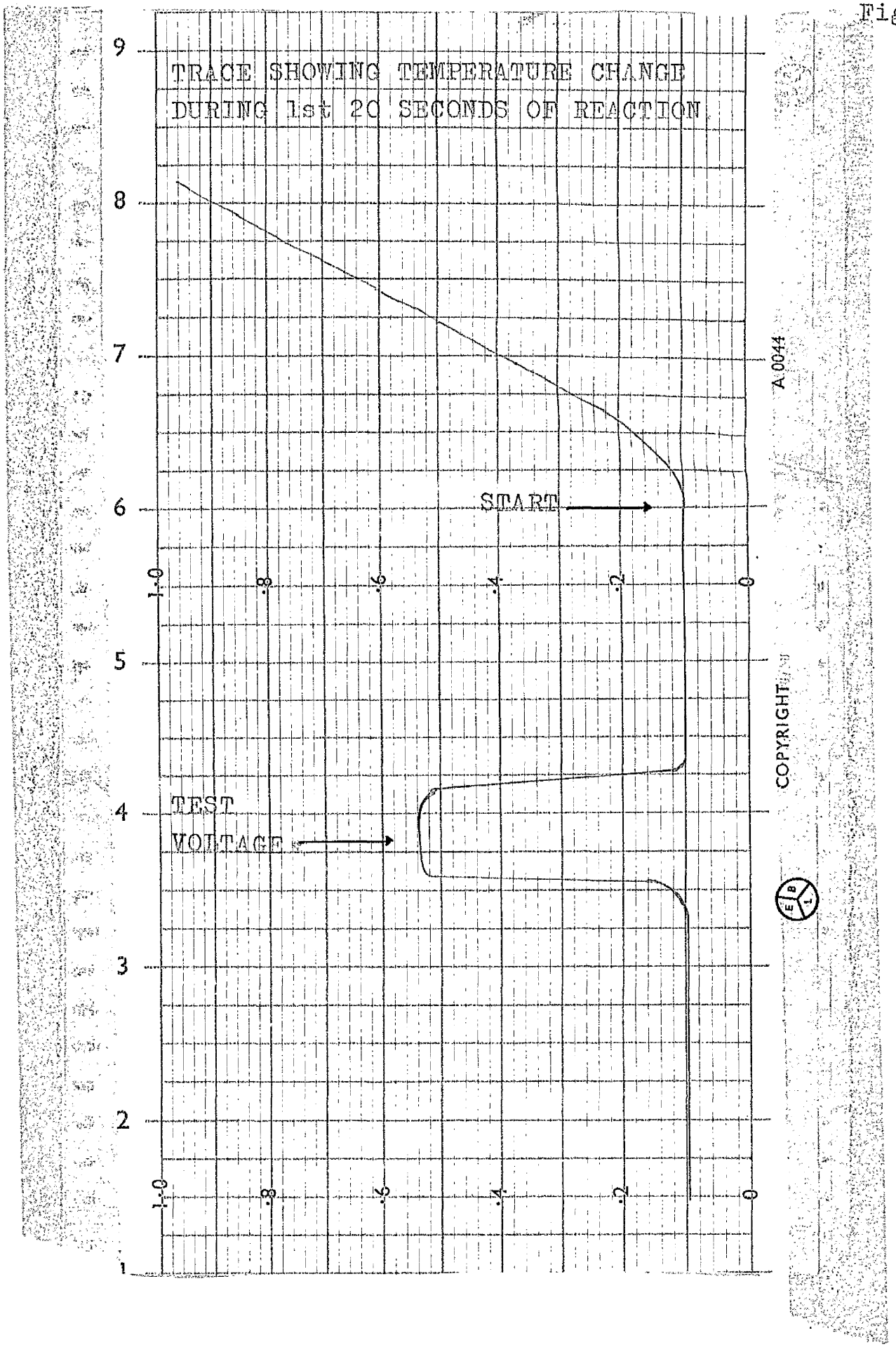
Now, slope of 1/Rate against X graph gives the ratio:- K_t/K_p.ln.2

$\therefore$ from Fig.(27), K_t/K_p.ln.2 = 11.3 sec.μv.$^{-1}$sec.$^{-1}$

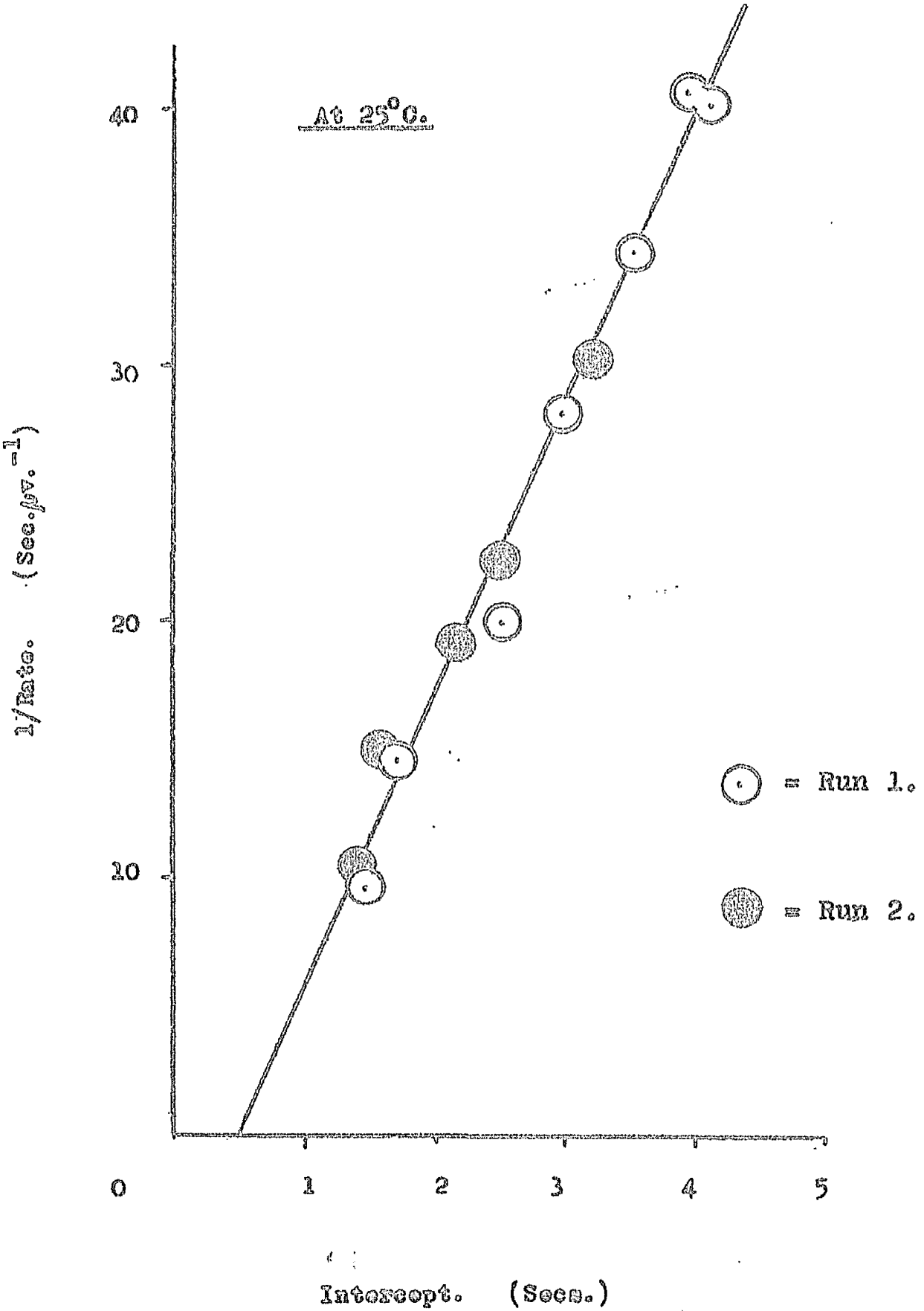
$$\therefore \quad K_t/K_p = \frac{11.3 \times 0.693}{8.6 \times 10^{-5}}$$

$$= 9.2 \times 10^{4} \text{ sec.}^{-1}$$

Fig.(26)


TRACE SHOWING TEMPERATURE CHANGE
DURING 1st 20 SECONDS OF REACTION
START
TEST
VOLTAGE
9
8
7
6
5
4
3
2
1
1.0
.8
.6
.4
.2
0
A 0044
COPYRIGHT

Graph of 1/Rate against intercept. Fig.(27)



Evaluation of rate of initiation.

Rate of polymerisation $\propto$ (Rate of initiation)$^{0.5}$

For a rate of poln. = 8.18×10^{-5} mole.l.$^{-1}$sec.$^{-1}$ the measured rate of initiation was 7.4×10^{-8} mole.l.$^{-1}$sec.$^{-1}$

$\therefore$ for a rate of poln. = 7.45×10^{-5} the rate of initiation is given by:-

$$\sqrt{I} = \sqrt{7.4 \times 10^{-8}} \times 7.45/8.18$$

$$\therefore \quad I = 6.15 \times 10^{-8} \text{ mole.l.}^{-1}\text{sec.}^{-1}$$

Now, from (1.10):-

$$\frac{K_p}{K_t^{0.5}} = \frac{-d\,M/dt}{I^{0.5}\,M}$$

$$= \frac{7.45 \times 10^{-5}}{2.48 \times 10^{-4} \times 9.3}$$

$$= 0.0324$$

Now, $K_t/K_p \times K_p/K_t^{0.5} = K_t^{0.5}$

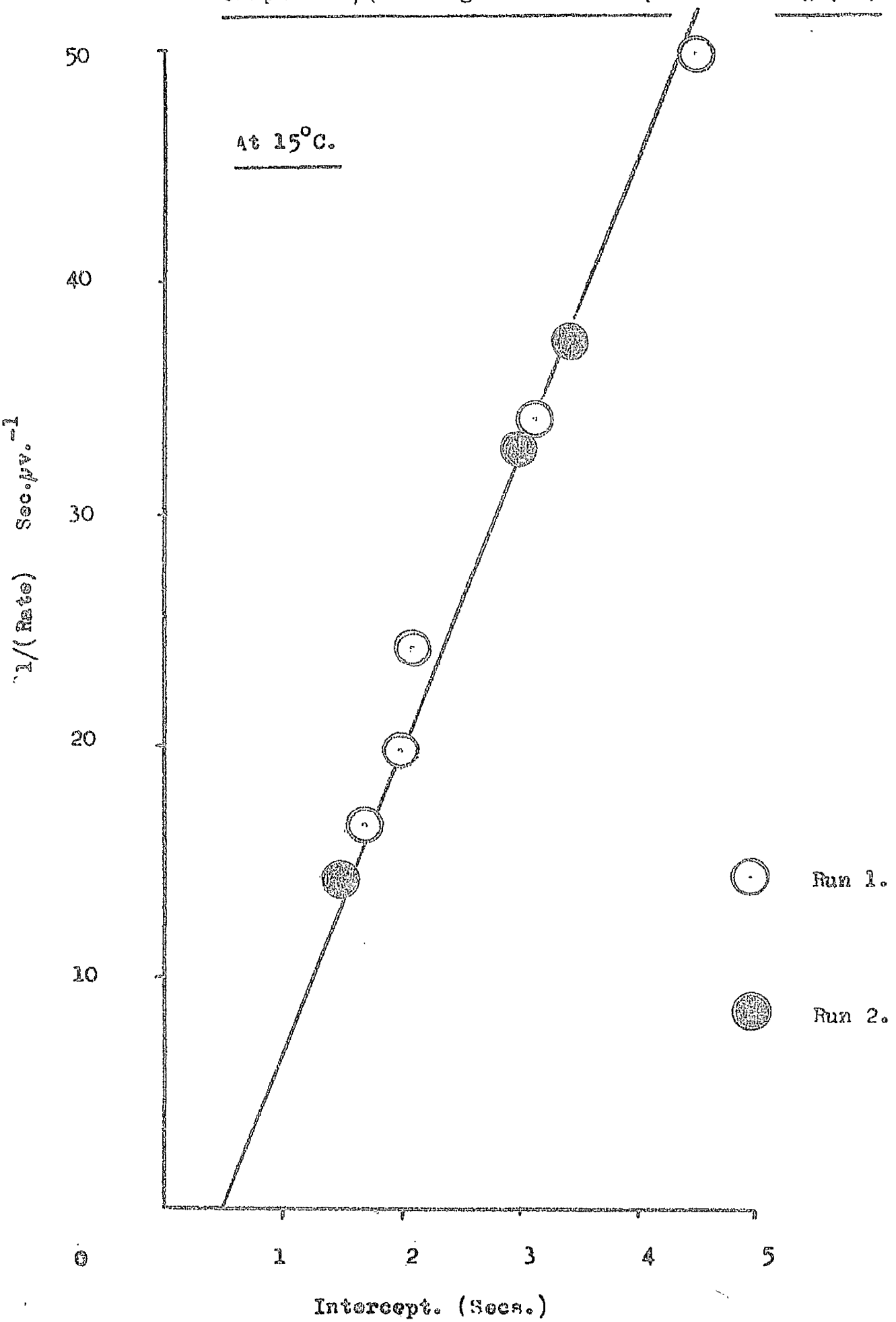
$\therefore \quad K_t^{0.5} = 2.98 \times 10^3$

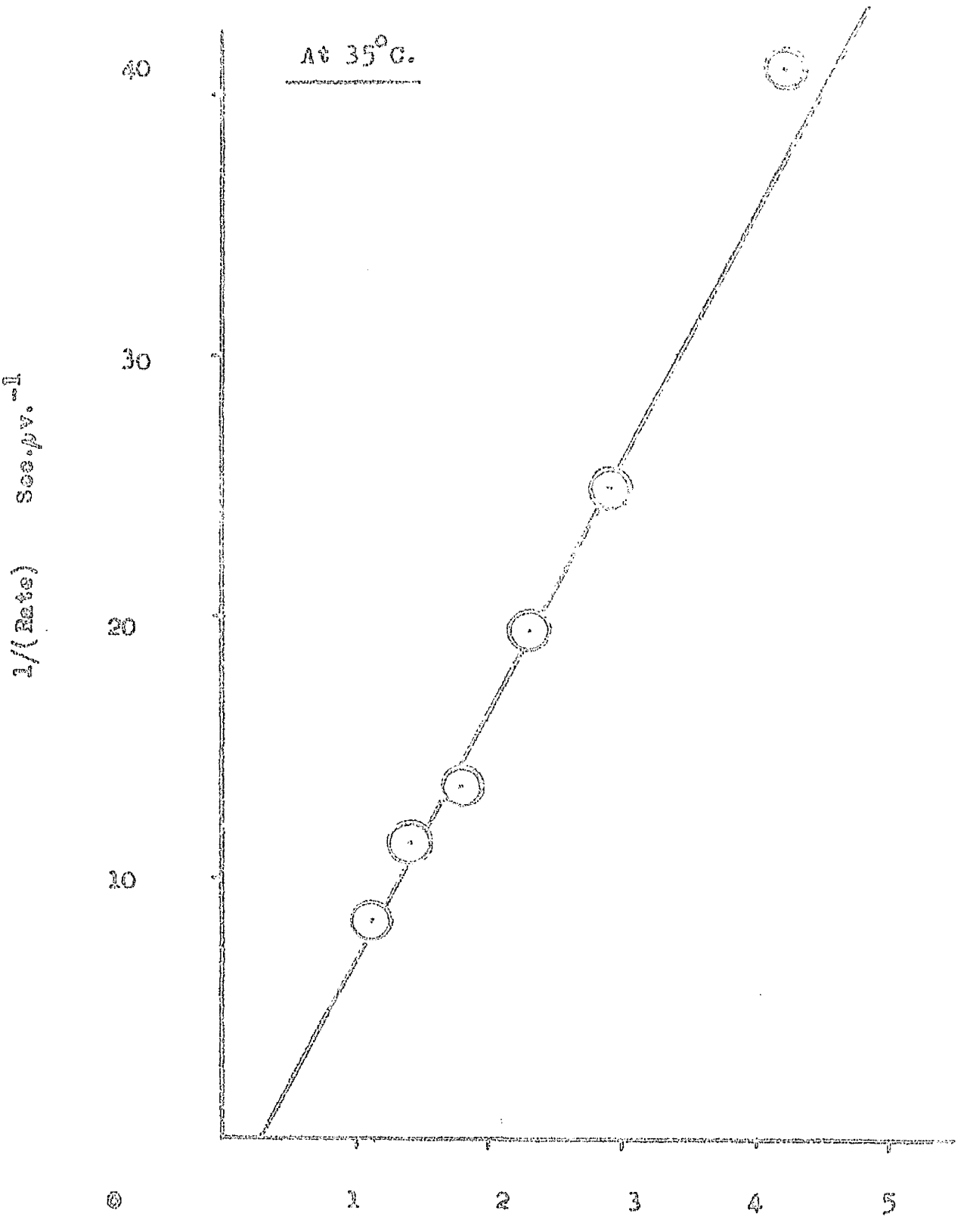
$\therefore \quad K_t = 8.9 \times 10^6$ mole.$^{-1}$ l.sec.$^{-1}$

and $K_p = 96.5$ mole.$^{-1}$l.sec.$^{-1}$

Graph of 1/(Rate against intercept

Fig.(28)




At 35°C.
40
30
20
10
0
1
2
3
4
5
1/(Rate) Sec.μv.⁻¹
Intercept (Secs.)

Evaluation of K_p and K_t by the rotating sector method.

The curve showing the variation of the ratio (rate at intermittent illumination)/(rate at full intensity) against the flash time is shown in Fig,(30)

For the sector used, the above ratio has the value of 0.694 when the flash time corresponds to the radical lifetime.

Thus, at 25°C, the value of τ from this curve is 0.7 seconds.

Now, from (5.4):

$$\tau = 1/(I.K_t)^{0.5}$$

$$\therefore K_t = 1/(I.\tau^2)$$

$$\therefore K_t = 1/(6.15 \times 10^{-8} \times 0.49)$$

$$= 3.3 \times 10^7 \text{ mole.}^{-1}\text{l.sec.}^{-1}$$

and hence $K_p = 186 \text{ mole.}^{-1}\text{l.sec.}^{-1}$

Comparison of the ratio K_p/K_t by thermocouple and sector methods.

By thermocouple method, $K_p/K_t = 11 \times 10^{-6}$

by sector method, $K_p/K_t = 5.6 \times 10^{-6}$

Fig. 13

Determination of activation energy.

The effect of temperature on a chemical reaction is expressed by the Arrhenious equation:-

$$K = A.e^{-E/RT} , \qquad (7.4)$$

where K is the velocity constant of the reaction, A is the frequency factor, representing the total frequency of encounters between the reacting species, E is the energy of activation for the reaction, T is the temperature at which the reaction occurs, where T is in degrees absolute, and R is the molar gas constant.

It has been shown that the rate of polymerisation can be expressed:-

$$\text{rate} = \frac{K_p \cdot I^{0.5}[M]}{K_t^{0.5}} \qquad (1.10)$$

$$\text{or,} \quad \text{rate} = \frac{K_p \cdot K_i^{0.5}[C]^{0.5}[M]}{K_t^{0.5}} \qquad ...(7.5)$$

where K_i is the velocity constant for the initiation reaction and C is the concentration of initiator.

$$\text{Let } K_o \text{ be equal to } K_p/Ki^{0.5}/K_t^{0.5} \qquad ...(7.6)$$

Then, (7.5) may be rewritten:-

$$\text{Rate} = K_o C^{0.5} [M] \quad \ldots(7.7)$$

$$\text{and,} \quad K_o = A.e^{-E_o/RT} \quad \ldots(7.8)$$

where E_o is the overall activation energy, and has the value:-

$$E_o = E_p + 0.5E_i - 0.5E_t \quad (7.9)$$

where E_p, E_i, and E_t represent the activation energies for propagation, initiation and termination respectively.

The overall activation energy can be found by plotting a graph of log(reaction rate) against 1/T

In a photochemically initiated polymerisation E_i is zero, so that (7.9) becomes:-

$$E_o = E_p - 0.5E_t \quad \ldots(7.10)$$

The individual values E_p and E_t may be found if K_p and K_t are known at one temperature, and their ratio at several other temperatures.

Fig.(31) shows a graph of log(reaction rate) against 1/T for the temperature range 15°C to 45°C. From this plot, the overall activation energy, E_o, is given by:-

$$E_o = \text{slope}/2.303RT$$

$$\therefore \quad E_o = 5.5 \text{ K.cal.mole}^{-1}$$

$\log_e(\text{Ratio})$ vs $1/T$
2.4
2.0
1.6
1.2
0.0032
0.0033
0.0034
0.0035

A graph of $\log.(K_t/K_p)$ against $1/T$ was drawn for the range $15^{o}C$ to $35^{o}C$. This is shown in Fig.(32) The activation energy, E_x, as given by this plot corresponds to:-

$$E_x = E_t - E_p \qquad \ldots(7.11)$$

From Fig.(32), $E_x = -3$ K.cal.mole.$^{-1}$

Therefore,

$$E_p = 8 \text{ K.cal.mole.}^{-1}$$

$$E_t = 5 \text{ K.cal.mole.}^{-1}$$

Measurement of the heat of polymerisation.

The normal methods for the determination of the heat of polymerisation are based on isothermal[68] or adiabatic calorimetry.[69 - 71] A further method given by Bengough[72] may also be used for radiation - induced reactions. This method does not readily fall into either of the two above categories. It depends on the measurement of the rate of polymerisation dilatometrically under conditions which may be described as a "thermal steady state" where the rate of self heating due to the reaction is balanced by the rate of loss of heat to the surroundings.

In this work the heat of polymerisation has been

Graph of $\log.(K_t/K_p)$ against 1/T.

Fig.(32)

determined the other method given by Bengough[71] in which the rate of rise of temperature under adiabatic conditions is equated to the rate of polymerisation as measured dilatometrically.

By confining the measurements to the first 20 seconds of the onset of polymerisation it is possible to avoid the use of elaborate thermal insulation or the application of cooling corrections to the results, since during this period the reaction is essentially adiabatic in character.[56]

It has been shown[56] that the polymerisation reaction occuring at the centre of a reaction vessel of the type used in this work remains adiabatic for at least 10 seconds, and in some cases up to 30 seconds after the start of the reaction. This is because the heat generated by reaction must eventually be conducted through the walls of the vessel and hence cooling is slowest at the centre of the dilatometer.

The variation in temperature with time during the first 20 seconds of reaction must be that which would occur under adiabatic conditions , and therefore it is possible to calculate the heat of polymerisation as shown on page 131 .

Specific heat.

A knowledge of the specific heat of the monomer is necessary to enable the heat of polymerisation to be evaluated. The specific heat of 2 - vinyl pyridine was found as described on page 113 by comparing the rate of cooling of equal volumes of 2 - vinyl pyridine, benzene, and carbon tetrachloride, the specific heats of the latter two liquids being known accurately.

15 cc samples of the liquids were used and the rate of cooling between 30°C and 25°C was observed. The half-life of cooling for each of the liquids was calculated from the cooling curves, the rates of cooling being compared at 27.5°C

The specific heats of benzene and carbon tetrachloride are 0.414 and 0.201 cal.gm.$^{-1}$ respectively, and the following half-life of cooling times were obtained.

2 - vinyl pyridine	15 mins.
benzene	9 mins.
carbon tetrachloride	7.5 mins.

Using relationship (6.1) the specific heat of 2 - vinyl pyridine was calculated to be 0.56 cal.gm.$^{-1}$

A typical cooling curve is shown in Fig.(33)

30
29
28
27
26
25
°C
0
10
20

Evaluation of the heat of polymerisation.

For 2 - vinyl pyridine:-

Molecular weight = 105

Specific heat = 0.56 cal.gm.$^{-1}$

Let ΔH = heat of polymerisation.

∴ Temperature rise for complete polymerisation of 1 mole under adiabatic conditions would be:-

$$t = \Delta H/(105 \times 0.56)\ ^{o}C.$$

Thus for a rate of polymerisation of 1% per hour, the rate of temperature rise would be:-

$$\Delta H/(105 \times 0.56 \times 3600)\ ^{o}C.sec.^{-1} \quad \therefore (7.12)$$

Since the rate of temperature increase and the rate of reaction can be measured, ΔH can be evaluated.

In a typical determination, the following data was found:-

Rate of polymerisation = 2.88% per hour

Rate of temperature rise = 0.0933/40 $^{o}C.sec.^{-1}$ (73)

∴ from (7.12) ΔH = 17.3 K.cal.mole.$^{-1}$

In table (12) some other heat of polymerisation determinations are given. The values of ΔH calculated assume that the specific heat of the monomer is the same over the range 15^{o}C to 35^{o}C.

Table (12)

Heat of Polymerisation.

Poln. conditions	Rate of poln. % per hour	Temp. rise μv.sec.$^{-1}$	Δ H.
25°C	2.68	0.0933	17.3
25°C (screen)	1.95	0.066	17.7
15°C	1.85	0.059	17.3
35°C	3.90	0.122	17.1

Δ H is in K.cal.mole.$^{-1}$

Summary of data on 4 - vinyl pyridine.

As only a small amount of 4 - vinyl pyridine was available, and time was limited, the results listed below should be regarded as preliminary observations, rather than finally established values.

All experimental techniques were the same as for 2 - vinyl pyridine, except that the polymer was precipitated from chloroform solution by adding toluene.

% Contraction - % Polymerisation relationship.

Only two determinations were made:-

Dilatometer volume	2.85 cc.	4.00 cc.
% Contraction	1.43 %	1.39 %
Time of reaction	120 min.	120 min.
Wt. of Polymer	0.2021 gm.	0.2911 gm.
% Polymerisation	7.54 %	7.43 %
.. 1% C =	5.25 % P	5.35 % P
Rate of polymerisation	3.77 %/hr.	3.71 %/hr.

An average value of 1% C = 5.3% P has been used.

Specific heat.

This was measured in the manner previously described on p.130. The half - life of cooling for equal volumes of benzene, carbon tetrachloride, and 4 - vinyl pyridine was determined, and since the specific heat of the first two liquids was known, the specific heat of 4 - vinyl pyridine could thus be found. By measurement, specific heat of 4 - vinyl pyridine is 0.50 $cal.gm.^{-1}$

Evaluation of constants for propagation and termination.

Due to the presence of an appreciable dark rate

at 35°C and a gel effect at 25°C at between 10% to 20% reaction, results are given only for reaction at 25°C and these apply over the range 2% to about 8% reaction.

In this work it has been assumed that the rate of initiation with 4 - vinyl pyridine was the same as the rate of initiation with 2 - vinyl pyridine, under the same conditions.

Data:

Rate of poln., measured dilatometrically = 3.8%/hr

Rate of poln., by nss method = 0.16μ v.sec.$^{-1}$

.. a rate of 1μ v.sec.$^{-1}$ = 6.6×10^{-1} sec.$^{-1}$

Fig.(34) gives the 1/Rate - X graph, and this has a slope of 4.4 sec.μv.$^{-1}$sec.$^{-1}$ = K_t/K_p.ln2.

Thus, as before,

$$K_p = 4 \times 10^6 \text{ mole.}^{-1}\text{l.sec.}^{-1}$$

$$K_t = 87 \text{ mole.}^{-1}\text{l.sec.}^{-1}$$

Evaluation of heat of polymerisation.

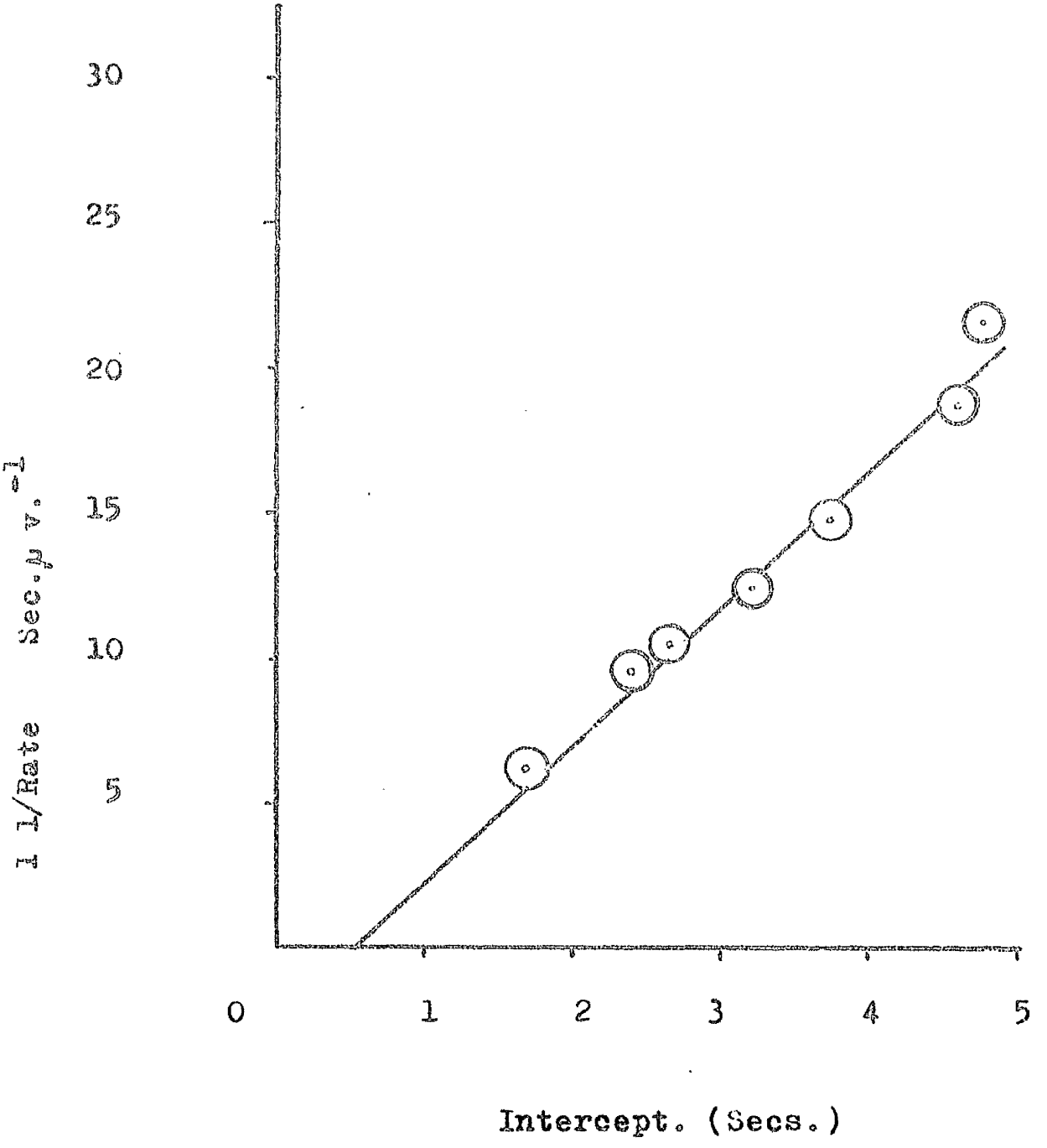
From the above rate measurements by the thermocouple and dilatometric methods, and using the method set out on p.131,

Heat of polymerisation = 19.8 K.cal.mole.$^{-1}$

Graph of 1/(Rate) against intercept Fig.(34)

for 4 - vinyl pyridine.

At 25°C.



C H A P T E R 8.

DISCUSSION.

The results obtained for the kinetic constants must be interpteted in the light of possible experimental errors and with due regard to the practical limitations which have been imposed by the methods used.

Some of the other methods which have been used by various workers to evaluate the velocity coefficients have a greater sensitivity than the non - stationary state thermocouple technique. Thus, Grassie & Melville's refractometric method [63] can detect a temperature change of 10^{-4} °C in 10^{-2} cec., while the dielectric constant method can give a temperature resolution of 10^{-5} °C in 10^{-4} sec.

The greater sensitivity of temperature measurement should enable more accurate measurements to be taken

during the non - stationary state period of the reaction and it should therefore be possible to determine the kinetic chain lifetime, τ , with greater precision. The greater sensitivity of temperature resolution is in practice offset by the greater experimental difficulty and by the need for more complex equipment than is needed in the non - stationary state thermocouple method.

Of the methods which are available for evaluating kinetic constants, the thermocouple technique is probably the most useful method to use. There are however certain difficulties and limitations in its use, as there must be in all such systems.

Sources of error in the thermocouple method.

Temperature measurement.

The temperature was recorded by the thermocouple at the centre of the reaction vessel. It has been assumed that the temperature of the bath in which the vessel was immersed remained constant. In practice this was not found to be the case. The signal received by the pen recorder was due to the opposing emfs. from the two thermojunctions, i.e., the cold junction in the vacuum jacket and the junction at the centre of the vessel. These were separated by a distance of

about 4 cm., and when the bath was being stirred there was an apparent temperature fluctuation of 0.005°C. When the stirrer was switched off the temperature apparently remained steady for a period of at least two minutes when the bath was at 25°C. There was thus ample time to obtain a trace of the reaction over a period of at least 30 secs. The accuracy of the method is thus somewhat greater than would seem probable at first sight.

The noise level of the amplifier corresponded to a temperature fluctuation of 0.000014°C and this represents the ultimate limit of temperature measurement.

The emf. - temperature relationship was obtained from the literature and was quoted at 25°C. In other systems the rate of reaction as measured by the thermocouple method has been found to be in good agreement with dilatometric measurements and close agreement has also been obtained by Bengough & Melville using platinum - platinum-rhodium thermocouples[56] thus indicating the reliability of the emf.-temperature relationship.

Taking all these factors into consideration the practical limit of temperature measurement is probably about 0.001°C.

Measurement of the lifetime.

There is always the possibility of inaccuracy in the extrapolation of the stationary state - time curve. The start of the reaction was determined visually. This procedure could well lead to an error of $\pm$ 0.1 sec. in the length of the lifetime, and would probably be constant from run to run. This type of error is dependent on personal response and the author considers that in his case the measured lifetime will tend to be too short. It was found necessary to use this somewhat unsatisfactory method of indicating the start of the reaction in contrast to the more usual procedure of using the pip produced by the operation of an electromagnetic relay controlling the shutter, since the large amplification which was required to follow the polymerisation of 2 - vinyl pyridine resulted in the emf.-time curve being distorted when the relay was used.

It is the variation of the instrument lag from run to run which results in the greatest errors. The response of the amplifier is 0.04 sec. and due to its small heat capacity the response time of the the thermocouple will also be very short. The lag of the pen recorder is very much greater, and can vary with the amount of ink in the pen reservoir.

To obtain an accurateestimate of the lifetime of the kinetic chain (to $\pm$ 0.1 sec.) under these conditions would require the lifetime to be of the order of three seconds. In fact most of the lifetimes measured were shorter than this, and it was necessary to repeat each determination several times to ensure that a reliable value was obtained for the lifetime. In the estimation of the intercept on the time axis in the emf. - time curve there was a variation of up to $\pm$ 20% in successive determinations of the same reaction. The points which are plotted in the 1/Rate against intercept graphs (Figs. 27 - 29) are the average of at least six separate determinations. In Fig.(27) the intercept on the time axis corresponding to the instrument lag is 0.5 sec. and it is seen that this could vary by about $\pm$ 0.2 sec., although the slope of the graph would only be slightly altered, in fact by about 4%. This indicates that the error in the ration of K_t to K_p as found from the slope of Fig.(27) is $\pm$ 4%, which is a much more accurate estimate of K_t/K_p than could be found from the trace of a single reaction.

Sources of error in the sector method.

It will be noted that there is a considerable difference in the constants derived by this method

compared with those found by the non - stationary state thermocouple method. The experimentally determined value of the kinetic chain lifetime, τ , is about half the value observed in the thermocouple method. Reference to Fig.(30) which shows the experimental relationship between R'/R_s' and the flash time indicates that at low sector speeds this ratio is rather lower than the theoretical value. Rate measurements were made using the thermocouple method. It is suggested that at slow sector speeds the reaction vessel does not remain adiabatic for a sufficiently long period to enable a true estimate of the reaction rate to be made, but that some heat evolved is lost to the water bath. A lower rate of reaction is thus obtained and the ratio R'/R_s' is in consequence reduced, thus giving a value of τ which is too small.

An alternative method of rate measurement would possible have enabled a better determination of τ , but simple dilatometric measurements were ruled out since a considerable amount of polymer formation would be involved in defining the experimental curve.

The darkening in colour of the monomer - polymer mixture which occurs at higher conversions would also tend to reduce the ratio R'/R_s' and τ , while

the gel effect at still higher conversions would cause an apparent increase in these values.

The polymerisation of 2 - vinyl pyridine.

Fig.(20) shows the graph of rate of polymerisation against $\sqrt{AIBN}$, while Fig.(22) shows the dependence of the rate of reaction on the intensity of irradiation. Within experimental error the rate of polymerisation is proportional to $\sqrt{AIBN}$ and $\sqrt{intensity}$, thus indicating that over the first few percent reaction the polymerisation conforms to the kinetic analysis set out in pages 4 - 6.

Fig.(23) shows a plot of $1/\overline{DP}_n$ against $\sqrt{AIBN}$. Only a few molecular weight determinations were made and accordingly too much emphasis should not be placed on these results. The line has been drawn passing through the origin, which would indicate that there is no monomer chain transfer. In view of the difficulties and errors associated with molecular weight determinations it is not unreasonable to suppose that the line as drawn is a fair representation of the relationship between $1/\overline{DP}_n$ and $\sqrt{AIBN}$. The dotted line in Fig.(23) indicates the maximum amount of chain transfer which may occur. The intercept on the $1/\overline{DP}_n$ axis corresponds to a value of 3×10^{-5} for the ratio K_{tr}/K_p , so that the constant for

monomer chain transfer in 2 - vinyl pyridine may have a value of up to $K_{tr} = 2.9 \times 10^{-3}$ mole.$^{-1}$l.sec.$^{-1}$

It is instructive to compare this value with the corresponding value for the monomer styrene, which is structurally similar to 2 - vinyl pyridine. At the same temperature, the transfer constant for styrene lies within the range $6 - 8 \times 10^{-4}$ mole.$^{-1}$l.sec.$^{-1}$ [74 - 76] but the ratio K_{tr}/K_p in styrene is slightly greater than the value of this ratio in 2 - vinyl pyridine, thus suggesting that chain transfer occurs rather less frequently in 2 - vinyl pyridine than it does in styrene. Onyon[54] gives a value of $K_{tr} = 8 \times 10^{-3}$ for 4 - vinyl pyridine.

A thermal dark rate has been observed in the polymerisation of 2 - vinyl pyridine; that is some reaction occurs due to the formation of radicals from the pure monomer which can then initiate growth of a chain in the absence of any irradiation. The extent of this reaction is initially very small compared with the rates of polymerisation in sensitised reactions at 15°C and 25°C, although at higher temperatures this dark reaction will increase as also will the thermal decomposition of the initiator. Rate measurements were therefore confined to the range 15°C to 45°C.

The reason for this dark rate is not clearly

understood although the reactivities of the monomer and polymer are probably important factors. Dark rates are also shown by some other monomers, but there has been little fundamental work done on this subject. Matheson et al.[77] in 1949 stated that there is a dark rate in styrene, and the rotating sector technique was modified to take account of the dark rate. A dark rate has also been reported by the above workers and by Bamford & Dewar[78] in the polymerisation of methyl methacrylate. Matheson et al.[79] in 1951 have also indicated that there is a dark rate in methyl acrylate. In a preliminary study of 4 - vinyl pyridine it was indicated that this monomer shows a dark rate which is greater than the dark rate in 2 - vinyl pyridine.

There are two opposing effects which occur during the polymerisation of the monomer as the reaction proceeds. These are:-

1) the darkening in colour of the monomer - polymer mixture which occurs at about 8% conversion; and

2) the gel effect which occurs at still higher conversions.

In 2 - vinyl pyridine a slight darkening of the colour occurs at about 8% reaction and there is a slight falling off in the rate of the reaction, and

the optical transmission of the solution decreases slightly. After a further few percent reaction no further darkening of colour takes place.

Evidence has also been found to suggest the presence of the "gel effect". This is the term normally used to describe the increase in the rate of polymerisation which occurs after the reaction has proceeded for some time at the normal rate. The gel effect is particularly pronounced in methyl methacrylate while in styrene the gel effect is very slight. 2 - vinyl pyridine lies between these monomers. The effect is usually explained in terms of a reduction of the rate of diffusion of polymer radicals such that the rate of mutual termination is reduced. At high viscosities the growing radicals are less mobile and thus the interaction of growing radicals is hindered, but the propagation reaction, which involves only one large growing radical, will be less affected and hence the overall effect will be an increase in the rate of polymerisation. The occurence of a gel effect in a monomer is conditioned by the properties of the polymer and the viscosity of its solution rather than resonance factors.

In table (13) given below the velocity coefficients obtained by several workers are shown for styrene. In

this table, which is taken from " The kinetics of vinyl polymerisation by radical mechanisms " by Bamford *et al.* the results of the original workers have been rationalized on the basis of termination by combination and in all cases K_t is defined by

$$- dR'/dt = K_t [R']^2$$

Table (13)

Velocity coefficients for styrene.

	Bamford & Dewar (74)	Burnett (76)	Melville & Valentine (75)	Matheson *et al.* (79)	Barb. (80)
K_p	18.7	19.7	26	44	24
$10^{-7}.K_t$	0.28	0.30	0.52	4.75	1.4
Temp. ^oC	25	25	30	25	20

In the original work disproportionation was assumed by Bamford and Dewar[74], Melville & Valentine[75], and Burnett[76]. Matheson *et al.* [79] took the rate of initiation as twice the rate of decomposition of the initiator and indicated that this assumption was in accord with inhibitor and molecular weight studies. Barb's work was based on Matheson's findings.

Bamford & Dewar[74] used the viscosity method to obtain the constants while Burnett[75] made use of measurements during the pre effect in the unsensitised photopolymerisation. Melville & Valentine[75] and Matheson et al[79] used the rotating sector technique. Barb[80] derived his values from a study of the co - polymerisation reaction of styrene with sulphur dioxide.

It will be seen that there is a wide scatter of results in table (13). This may be due to experimental difficulties assosiated with some of the methods used, or to the use of assumptions which are not completely justified. A further factor responsible for lack of better agreement is the possibility of the presence of traceimpurities in the monomer used. The difference in the results obtained by Melville & Valentine[75] and Matheson et al[79] is surprising in view of the fact that they used the same method.

The velocity coefficients derived for 2 - & 4 - vinyl pyridines are given below:-

2 - vinyl pyridine:

thermocouple method - $K_p = 96.6$ $K_t = 8.9 \times 10^6$

sector method - $K_p = 186$ $K_t = 3.3 \times 10^7$

4 - vinyl pyridine:

thermocouple method - $K_p = 87$ $K_t = 3 \times 10^6$

4 - vinyl pyridine:

Onyon's results[54] — $K_p = 12$ $k_t = 3 \times 10^6$

For the purposes of comparison the constants for some of the common monomers are listed in table (14).

Table (14).

Velocity coefficients for some common monomers.

Monomer.	Temp.	K_p	K_t	Reference.
vinyl acetate	25°C	1012	5.9×10^7	Matheson.[81]
vinyl acetate	25°C	1100	8×10^7	Swain & Bartlett[62]
methyl acrylate	30°C	720	413×10^6	Matheson[82]
methyl acrylate	25°C	1580	5.5×10^7	quoted in 30
m. methacrylate	24°C	310	6.6×10^7	Mackay & Melville[84]
m. methacrylate	30°C	286	2.4×10^7	Matheson.[83]
styrene	25°C	44	4.8×10^7	Matheson.[79]
butyl acrylate	25°C	13	1.8×10^4	Melville & Bickel.[85]
p-methoxystyrene	0°C	2.9	5.8×10^5	Axford.[86]

The difference in the constants found by the two methods used in this work for the monomer 2 - vinyl pyridine has already been pointed out, and considering the various errors involved, the result by the

thermocouple method is probably the more accurate.

Table (14) indicates that vinyl acetate has the highest value of K_p. The radical formed from this monomer is very reactive, mainly because it lacks strong resonance stabilization, while the styryl radical on the other hand is relatively more stable the the vinyl acetate radical, as is indicated by the lower K_p for styrene.

The results which have been found in this work indicate that both 2 - and 4 - vinyl pyridine are intermediate in activity between vinyl acetate and styrene, and show greater similarity to styrene than to vinyl acetate. It would appear that the values of K_p found for the vinyl pyridines are definitely higher than any of the values of K_p for styrene given in table (13) thus indicating that these monomers are slightly less reactive than styrene, although the radicals will be correspondingly more reactive. It is interesting to note in this connection that the monomers which have been reported as having a thermal dark rate are the monomers which form reactive radicals.

While insufficient work was done to establish the constants for 4 - vinyl pyridine conclusively, it would seem that Onyon's value[54] of 12 for K_p is rather low. Later workers have found relationships between intrinsic viscosity and molecular weight which disagree

considerably with the relationship derived by Onyon. (Boyes & Strauss[87] and Fuoss et al.[88])

It is seen that within experimental error the constants derived for both 2 - vinyl pyridine and 4 - vinyl pyridine by the thermocouple method are similar, but the termination constant of 4 - vinyl pyridine is definitely smaller than the constant for 2 - vinyl pyridine. The termination process is thus faster in 2 - vinyl pyridine and this is reflected in the rate of polymerisation being slower than in 4 - vinyl pyridine.

The heat of polymerisation for 2 - vinyl pyridine has been evaluated in this work and a preliminary estimate has been made of the heat of polymerisation of 4 - vinyl pyridine. Joshi[89,90] has recently described a refined technique for evaluation of heats of polymerisation based on isothermal calorimetry. His values for 4 - vinyl pyridine[89] and 2 - vinyl pyridine[90] are in good agreement with the values found in this work:-

4 - vinyl pyridine ----	Joshi[89]	18.70 ± 0.28
	this work	19.8
2 - vinyl pyridine ----	Joshi[90]	17.1 ± 0.1
	this work	17.3 ± 0.3 , the

units being K.cal.mole.$^{-1}$

The difference of 1.6 K.cal.mole.$^{-1}$ between 2 - vinyl pyridine and 4 - vinyl pyridine found by Joshi[89,90] indicates a difference in resonance energy of this amount.

It is seen that the heat of polymerisation of the vinyl pyridines is slightly greater than the value of 16.5 K.cal.mole.$^{-1}$ given for styrene by Joshi[89], which is in agreement with the propagation constants for the vinyl pyridines being greater than the propagation constant for styrene.

The radical formed from styrene monomer is stabilised due to the conjugation of the phenyl groups with the double bond, and this resonance stabilisation depresses the activity of the radical. The effect of the N atom in the vinyl pyridines is to reduce this resonance stabilisation so that the radicals formed are more reactive than the styryl radicals.

Tha activation energies for the propagation and termination reactions in 2 - vinyl pyridine are compared with some other well known vinyl monomers in table (15).

Table (15).

Activation Energies.

	2 - vinyl pyridine.	Styrene.[76]	Methyl methacrylate.[84]	Vinyl acetate.[91]
E_p	8	6.3	4.4	4.4
E_t	5	1.9	1.0	0
		Units: K.cal.mole.$^{-1}$		

The activation energies of 2 - vinyl pyridine have been evaluated over a short temperature range and hence they may reflect some inaccuracy. The values of E_p & E_t obtained are of a similar magnitude to most of the other monomers listed. E_p for both styrene and 2 - vinyl pyridine are very similar, although E_t appears to be significantly greater in 2 - vinyl pyridine.

Final conclusions: 2 - vinyl pyridine in the initial stages of polymerisation follows the kinetic scheme established on pages 4 - 6. It behaves in many ways like thevmonomer styrene, although the radical formed is somewhat more reactive than the styryl radical.

More work is necessary to establish fully the kinetics of the polymerisation of 4 - vinyl pyridine and such a study would be a logical extension of the work reported in this thesis.

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